SOLAR-DRIVEN SELF-SUSTAINED PHOTOELECTRIC CELL FOR GREEN HYDROGEN PRODUCTION

Dissertation submitted to
Visvesvaraya National Institute of Technology, Nagpur
In partial fulfilment of the requirements for the award of the degree

Master of Technology
in
VLSI DESIGN

by

Gudivada Chandra Mohan

(MT23MVD006)

Under the guidance of

Dr. Nikhil Deep Gupta

Center for VLSI and Nanotechnology
Visvesvaraya National Institute of Technology
Nagpur 440010 (India)
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Center for VLSI and Nanotechnology

Visvesvaraya National Institute of Technology, Nagpur

DECLARATION

I, **GUDIVADA CHANDRA MOHAN**, hereby declare that this dissertation titled "**Solar-Driven Self-Sustained Photoelectric Cell for Green Hydrogen Production**" was carried out by me in the Department **of Center for VLSI and Nanotechnology** of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier, whole or in part, for the award of any degree/diploma at this or any other Institution / University.

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Date:

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This certifies that the dissertation titled "**Solar-Driven Self-Sustained Photoelectric Cell for Green Hydrogen Production**" is submitted by **Gudivada Chandra Mohan** in partial fulfillment of the requirements for the award of the degree of **Master of Technology in VLSI Design**, VNIT Nagpur. The work is comprehensive, complete, and fit for final evaluation.

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Abstract

The growing global energy needs and ecological challenges have intensified the search for clean, renewable, and sustainable energy sources. Hydrogen has emerged as a promising green energy carrier due to its high energy density and zero carbon emissions upon use. This project presents a novel solar-driven, self-sustained photoelectrochemical (PEC) system for green hydrogen production, integrating advanced nanomaterials with high-efficiency solar concentration. The core of the system involves two comparative configurations: one utilizing a conventional titanium dioxide (TiO_2) photoanode and the other employing an InGaN/GaN nanowire-based photoelectrode. Both setups are paired with platinum cathodes and a proton exchange membrane (PEM) within a sealed cubic PEC cell, using water and hydrobromic acid as the electrolyte.

The TiO_2-based system, known for its chemical stability and cost-effectiveness, offers moderate photocurrent performance but requires optimization to improve solar-to-hydrogen conversion. In contrast, the InGaN/GaN nanowire electrode demonstrates superior efficiency due to enhanced light absorption, excellent charge separation, and robust chemical resilience under concentrated solar illumination. A custom-designed solar dish concentrator array (diameter 4.97 m each) focuses solar irradiance with a mean deposited power of ~67.87 W, achieving a high concentration ratio (~24,000×) and delivering a photonic flux dense enough to trigger efficient water splitting.

The InGaN/GaN electrode configuration outperforms the TiO_2 counterpart in photocurrent density and operational stability, offering a promising pathway for future scale-up. This hybrid PEC system demonstrates a viable route toward sustainable, clean hydrogen production by leveraging nanostructured semiconductors and solar concentration technologies.This work demonstrates a compact, scalable, and eco-friendly system for decentralized hydrogen generation. Additionally, it offers the potential for concurrent wastewater treatment, contributing to circular economy principles. The proposed system paves the way for green hydrogen technologies and off-grid energy solutions, particularly in rural and resource-limited regions.

List of Figures

Figure 1: Global Ecosystem 2
Figure 2:Production of hydrogen using the Electrolysis Process 6
Figure 3: PEC System [18] 7
Figure 4: Solar Thermochemical Hydrogen Production 8
Figure 5: Microbial Electrolysis Cells [4] 9
Figure 6: Hydrogen Fuel Cell Cars 12
Figure 7: PEC Characterization Setup [2] 17
Figure 8: J–V curves of DSSCs with different counter electrodes and photoelectrodes [6] 22
Figure 9: PEM set up [13] 23
Figure 10: Electric dynamic model of a single PEM fuel cell [13] 23
Figure 11The simulated current (I_cell) of a PEMFC connected through a 4 mΩ wire to a 4 mH superconducting coil, illustrating the response when I_set changes abruptly from 15 A to 20 A. [12] 24
Figure 12a): working electrode. (source: DEK RESEARCH INSTRUMENTATION) 27
Figure 13b): Detailed parameter table of the electrode holder. (source: DEK RESEARCH INSTRUMENTATION) 28
Figure 14: working electrode using group III nitrides (InGaN/GaN) 29
Figure 15a): counter electrode (source: DEK RESEARCH INSTRUMENTATION) 32
Figure 16:b. Detailed parameter table of the counter electrode. (source: DEK RESEARCH INSTRUMENTATION) 33
Figure 17a): Reference electrode (source: DEK RESEARCH INSTRUMENTATION) 36
Figure 18: The detailed parameter table of the reference electrode (source: DEK RESEARCH INSTRUMENTATION) 36
Figure 19a): PEM 37
Figure 20b): Migration of H^+ ions from the anode to the cathode via the proton exchange membrane (PEM) [7]. 38
Figure 21: Electrolyte solution. 39
Figure 22a): quartz tube (source: DEK RESEARCH INSTRUMENTATION) 40

Figure 23: Detailed parameters of the Quartz tube (source: DEK RESEARCH INSTRUMENTATION) 40
Figure 24: Hydrogen tank 42
Figure 25: voltmeter and ammeter 43
Figure 26: PEC setup. 45
Figure 27:Ray Trajectories, Ideal Reflector 50
Figure 28: b) Ray Trajectories is the ideal reflector in the YZ direction 51
Figure 29:Deposited Power, Ideal Reflector 52
Figure 30:Concentration Ratios 53
Figure 31:Anode Hydrogen concentration 54
Figure 32:Cathode oxygen concentration 54
Figure 33:Cathode Hydrogen concentration 55
Figure 34: Anode H2O concentration 55
Figure 35: Membrane current density 56
Figure 36: Meshing on the solar receiver dish 57
Figure 37: Structure of Electrochemical Cell. 59
Figure 38: Current density vector of Photoelectrochemical cell 59
Figure 39: Pressure generated by hydrogen gas 60
Figure 40: Polarization curve 61

List of Tables

Table 1: List of semiconductors and band gaps 19

Table 2: DSSC Photovoltaic Properties Based on Different Counter and Photoelectrode Combinations 21

Contents

1 Introduction 2

1.1 Global Energy Scenario 2

1.2 Hydrogen as a Clean Alternative Fuel 3

1.3 Hydrogen in the Renewable Energy Industry 3

1.3.1 Methods of Hydrogen Production 4

1.3.2 The Future of Hydrogen 10

1.4 Role of PEC Cells and Solar Integration 12

1.5 Objectives of the Study 13

1.6 Scope of the Work 14

1.7 Thesis Organization 14

2 Literature Review 17

2.1 PEC 17

2.1.1 Overview of PEC Water Splitting 18

2.1.2 Titanium Dioxide (TiO_2)-Based Systems 18

2.1.3 Carbon-Based Photocatalysts and Doping Strategies 18

2.1.4 Composite Photoelectrodes and rGO-Based Counter Electrodes 18

2.1.5 Proton Exchange Membranes (PEMs) 19

2.1.6 III–V Semiconductor Materials 19

2.1.7 Technoeconomic and System-Level Analysis 19

2.1.8 PEC Systems Using Wastewater as Electrolyte 20

2.2 Material Innovations in PEC Cells 20

2.3 Composite Films and Nanostructures 20

2.4 Role of Proton Exchange Membranes (PEM) 22

2.5 PEMFC Modeling Framework 23

2.5.1 Superconducting Coil (SC) Model 24

2.5.2 System-Level Integration and Validation 24

2.6 Solar Concentrators and Self-Biasing 25
2.7 Hybrid Applications and Integration 25
2.8 Challenges Identified in Literature 25
3 DESIGN METHODOLOGY 27
3.1 Overview 27
3.2 Material specification 27
3.2.1 Working Electrode 27
3.2.2 Counter Electrode 31
3.2.3 Reference Electrode 34
3.2.4 Proton Exchange Membrane (PEM) 36
3.2.5 Electrolyte Solution 38
3.2.6 Quartz Tube 39
3.2.7 Storage of hydrogen gas 41
3.2.8 Voltmeter and ammeter 42
3.3 Connection of three electrodes with metal wires 44
3.4 PEC Cell Assembly 44
3.5 Working Principle 46
3.6 Effect of Operating Conditions 48
3.7 Summary 48
4 Theoretical analysis and performance calculations 50
4.1 Solar Dish Concentrators 50
4.2 Proton Exchange Membrane (PEM) Analysis 53
4.3 Integration of Solar Dish with PEC Cell 56
4.4 PEC Cell Geometry and Current Distribution 58
4.5 Polarization Curve and Fill Factor Calculations 60
4.6 Theoretical calculations 61

4.6.1 Hydrogen Generation Estimation Using Faraday's Law.....63

5 Conclusion and future work.....65

5.1 Conclusion.....65

5.2 Future Work.....66

6 REFERENCES.....68

List of Abbreviations

PEC – Photoelectrochemical Cell

PEM – Proton Exchange Membrane

PEMFC – Proton Exchange Membrane Fuel Cell

TiO_2 – Titanium Dioxide

Pt – Platinum

UV – Ultraviolet

H_2 – Hydrogen

O_2 – Oxygen

HER – Hydrogen Evolution Reaction

OER – Oxygen Evolution Reaction

AM 1.5G – Air Mass 1.5 Global (solar simulator standard)

DSSC – Dye-Sensitized Solar Cell

rGO – Reduced Graphene Oxide

SC – Superconducting Coil

KCl – Potassium Chloride

Ag/AgCl – Silver/Silver Chloride

STP – Standard Temperature and Pressure

STCH – Solar Thermochemical Hydrogen

HBr – Hydrobromic Acid

PV – Photovoltaic

STH – Solar-to-Hydrogen

ALD – Atomic Layer Deposition

g-C_3N_4 – Graphitic Carbon Nitride

1

INTRODUCTION

1 Introduction

1.1 Global Energy Scenario

The global energy sector is currently navigating a complex and urgent transition. In 2023, global primary energy consumption reached record levels, driven largely by oil and coal, which together accounted for over 60% of the energy mix. Despite renewables achieving their highest historical share at 15%, they remain insufficient to counterbalance rising fossil fuel use. The Global South, experiencing rapid industrialization and population growth, contributed significantly to this surge in energy demand. This growth has intensified carbon emissions, with CO_2 levels surpassing 40 gigatonnes, marking the highest annual emissions on record. Fossil fuels, particularly coal, are major contributors to global warming and air pollution. The continued reliance on these energy sources has already caused the average global temperature to increase by over 1°C, with the critical 1.5°C threshold being reached in 2024. This temperature rise threatens biodiversity, food security, and the stability of global ecosystems.

Figure 1: Global Ecosystem

(SOURCE: EARTH.ORG)

While some developed regions like the EU and the US have begun to reduce their fossil fuel consumption, global energy systems remain heavily dependent on coal, oil, and gas. Encouragingly, significant investments in clean energy technologies are underway, with $2 trillion forecasted in 2024. Countries like China are leading in renewable energy deployment, accounting for more than half of global additions. Nevertheless, the transition

remains uneven, and stronger international collaboration and policy support are essential to accelerate progress.

1.2 Hydrogen as a Clean Alternative Fuel

Hydrogen is the most abundant and simplest element in the universe, accounting for roughly 75% of all matter. It is a colorless, odorless, non-toxic, and highly reactive gas. As an energy carrier, hydrogen has gained tremendous attention in recent decades due to its potential to replace traditional fossil fuels across various sectors. It can be produced from a wide array of domestic sources such as natural gas, coal, biomass, nuclear energy, solar, and wind, making it a strategic component in achieving energy security and sustainability.

Its versatility extends across industrial, residential, and transportation sectors. In fuel cells, electrical power is produced by the electrochemical reaction of hydrogen and oxygen, resulting in water as the only waste product, resulting in zero harmful emissions. This positions hydrogen as a crucial enabler of decarbonization in the global energy transition.

Hydrogen serves as a critical feedstock in various industrial applications such as oil refining, metal processing, ammonia-based fertilizer manufacturing, and food industry operations. In the United States, nearly all hydrogen currently produced is consumed by such industries.

Within the energy domain, hydrogen is being adopted as an eco-friendly fuel replacement in gas-based power stations and for storing surplus energy from intermittent renewables like wind and solar. Fuel cell electric vehicles (FCEVs), hydrogen-powered buses, and hydrogen trains are already operational in several countries, signaling a future of sustainable transport powered by hydrogen.

1.3 Hydrogen in the Renewable Energy Industry

Hydrogen serves dual roles as both a fuel and an energy carrier. It enhances the flexibility and reliability of renewable energy systems by acting as a medium for energy storage and transport. This enables the smoothing of energy supply fluctuations from solar or wind sources. Through integration with fuel cells, hydrogen can generate electricity efficiently and be used to power buildings, remote installations, or electric vehicles.

In industrial settings, hydrogen is already instrumental in producing ammonia and removing sulfur from petroleum, and its role is expected to grow as green hydrogen production becomes more feasible.

Hydrogen is emerging as a cornerstone of the global energy transition. It offers a carbon-free fuel option with high energy content and clean combustion, emitting only water vapor and heat. Its adaptability makes it suitable for use in transportation, electricity generation, and industrial processes such as ammonia synthesis and steel production.

In transportation, hydrogen fuel cells enable rapid refueling and extended range, making them ideal for freight and long-distance travel. In industrial sectors, hydrogen serves as a cleaner feedstock, helping reduce reliance on carbon-intensive fossil fuels.

Hydrogen generation is possible from multiple sources such as fossil fuels like natural gas, organic matter like biomass, nuclear energy, and—critically—green electricity through the process of electrolysis. The method of production significantly affects its environmental impact. "Green hydrogen," derived via electrolysis powered by renewable energy, holds the greatest promise for a sustainable hydrogen economy.

1.3.1 Methods of Hydrogen Production

Hydrogen fuel production can be achieved through different technological methods, each falling under four main categories: thermal, electrolytic, solar-driven, and biological processes.

A. Thermal Processes: Thermal hydrogen production primarily relies on steam methane reforming (SMR), a high-temperature chemical reaction between steam and a hydrocarbon fuel, most commonly natural gas. This process is currently the most dominant method, accounting for approximately 95% of global hydrogen production.

Steam Methane Reforming (SMR) is the primary method used in thermal hydrogen production, where methane (CH_4) undergoes a high-temperature (700–1,000°C) reaction with steam under elevated pressure (3–25 bar) and in the presence of a nickel catalyst to yield hydrogen (H_2), carbon monoxide (CO), and trace amounts of carbon dioxide (CO_2).

The primary reactions involved are:

Steam Reforming Reaction:

$CH_4 + H_2O \rightarrow CO + 3H_2$

Water-Gas Shift Reaction:

$CO + H_2O \rightarrow CO_2 + H_2$

This method is the most widely adopted, accounting for approximately 95% of global hydrogen production. Other thermal methods include biomass gasification, where organic materials are converted into syngas (a mixture of H_2, CO, and CO_2) through partial oxidation at high temperatures, and reforming of renewable liquid fuels like ethanol or biodiesel, which undergo similar reactions to release hydrogen. While these processes are commercially mature, they are carbon-intensive unless integrated with carbon capture and storage (CCS) technologies to mitigate CO_2 emissions.

Despite its commercial maturity, thermal hydrogen production is carbon-intensive unless coupled with carbon capture and storage (CCS).

B. Electrolytic Processes: One of the most sustainable methods of producing hydrogen is through water electrolysis, where an electric current is used to split water molecules (H_2O) into hydrogen (H_2) and oxygen (O_2) using a device known as an electrolyzer. This process becomes carbon-neutral when powered by renewable energy sources such as wind or solar, producing what's commonly known as green hydrogen. There are several types of electrolyzers, including alkaline, PEM (proton exchange membrane), and solid oxide, each with its own set of features and efficiency ranges. The basic chemical reaction involved is:

Stargate Hydrogen

$2H_2O\ (l) \rightarrow 2H_2(g) + O_2(g)$

In this process, water molecules are decomposed into hydrogen and oxygen gases. When the electricity used is derived from renewable sources, the hydrogen produced is considered green, offering a carbon-free energy carrier. This method is gaining traction as a viable solution for large-scale clean hydrogen generation, especially as the cost of

renewable electricity continues to decline.

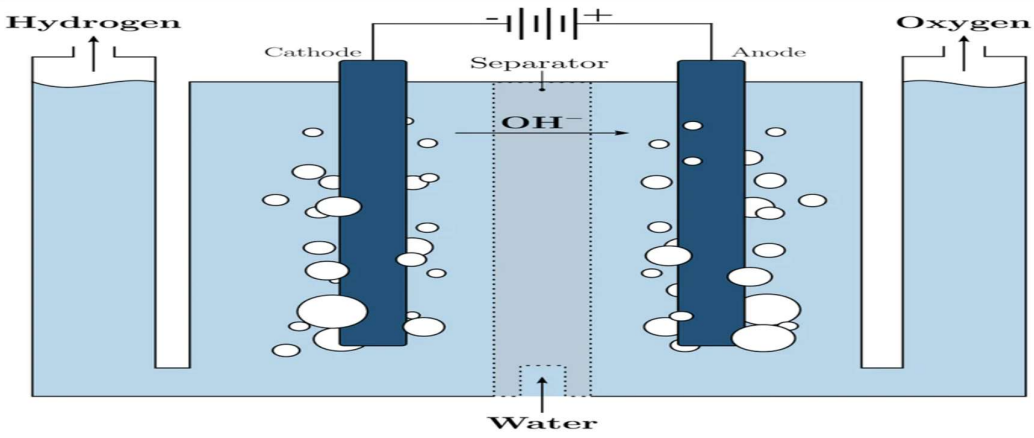


Figure 2:Production of hydrogen using the Electrolysis Process

(SOURCE: stargatehydrogen.com)

C. Solar-Driven Processes:

Solar-driven hydrogen production is a promising approach to generate clean energy by harnessing sunlight to split water molecules into hydrogen and oxygen. This process can be categorized into three main technologies:

1. Photobiological Hydrogen Production

Photobiological hydrogen production leverages the natural photosynthetic activity of microorganisms like algae and cyanobacteria to harness solar energy for hydrogen generation. Under anaerobic conditions or nutrient-limited environments, particularly sulfur or nitrogen deprivation, these organisms emit hydrogen as a part of their metabolic processes. While this approach holds significant promise for sustainable hydrogen production, its practical application is constrained by factors such as sensitivity to oxygen and the requirement for tightly regulated environmental conditions

2. Photoelectrochemical (PEC) Water Splitting

Solar-driven hydrogen production is a clean and sustainable energy solution that utilizes sunlight to split water molecules into hydrogen and oxygen. Among the various approaches available, photoelectrochemical (PEC) water splitting has gained considerable attention for its ability to integrate light absorption and electrochemical conversion in a single device. In a PEC system, sunlight excites a semiconductor photoelectrode,

generating electron-hole pairs that drive the water-splitting reaction, producing hydrogen at the cathode and oxygen at the anode.

In the initial phase of this project, a PEC cell was developed using titanium dioxide (TiO_2) as the working photoelectrode. TiO_2, known for its high chemical stability and corrosion resistance, served as a reliable material for water oxidation under UV illumination. Integrated with a proton exchange membrane (PEM) and a platinum counter electrode, the TiO_2-based setup demonstrated effective hydrogen generation. However, limitations in its optical absorption (restricted mostly to the UV region) and photocurrent output prompted further investigation into advanced materials.

To enhance solar energy utilization and improve PEC performance, the project progressed to using InGaN/GaN nanowire-based photoelectrodes. These semiconductor nanowires offer superior light absorption in the visible spectrum, along with enhanced surface area and improved charge separation efficiency. The nanowire architecture facilitates efficient electron-hole transport under solar irradiation, making it highly suitable for high-intensity light applications, such as those using solar dish concentrators. The PEC cell design was adapted to accommodate this nanostructured photoelectrode, aiming to achieve higher photocurrent density, improved hydrogen production rates, and better solar-to-hydrogen (STH) efficiency.

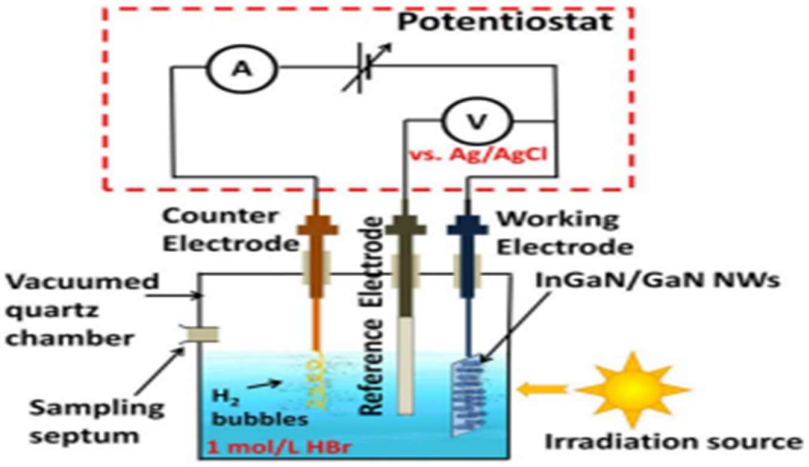


Figure 3: PEC System [18]

This evolution from TiO_2 to InGaN/GaN represents a critical step toward realizing high-performance, solar-driven PEC systems capable of contributing to large-scale green hydrogen production.

3. Solar Thermochemical Hydrogen Production

Solar thermochemical (STCH) hydrogen production employs concentrated solar power (CSP) to drive high-temperature chemical reactions that split water into hydrogen and oxygen, achieve high temperatures necessary for thermochemical cycles that split water into hydrogen and oxygen. These cycles typically involve metal oxide redox reactions, where an endothermic reaction absorbs solar heat to reduce metal oxides, and an exothermic reaction releases oxygen and produces hydrogen.

The process operates at temperatures ranging from 500°C to 2,000°C, utilizing solar thermal energy to drive the reactions. This method offers the advantage of producing hydrogen without the need for electricity and can be integrated with existing CSP infrastructure.

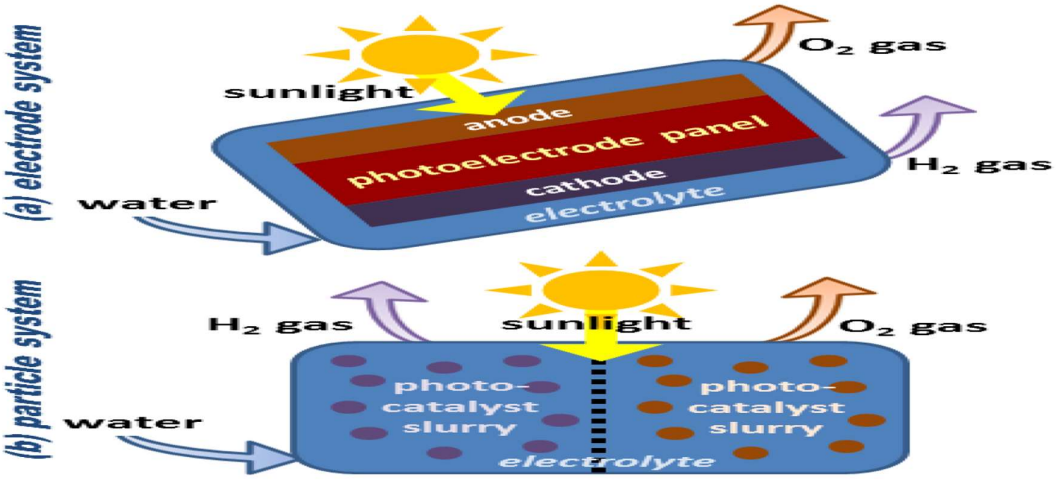


Figure 4: Solar Thermochemical Hydrogen Production

(Source: energy.gov.)

These processes represent cutting-edge technologies that merge solar energy with chemical conversion, with PEC methods being particularly promising due to their compact design and potential for direct hydrogen evolution.

D. Biological Processes: Photobiological hydrogen production involves photosynthetic microorganisms, such as algae and cyanobacteria, that generate hydrogen gas using sunlight. These organisms possess hydrogenase enzymes that facilitate the conversion of protons into hydrogen gas.

Green Algae (e.g., Chlamydomonas reinhardtii): Under anaerobic conditions and sulfur deprivation, these algae can produce hydrogen by decoupling photosynthesis from oxygen evolution. Cyanobacteria (e.g., Synechocystis sp.): These bacteria can produce hydrogen through nitrogenase activity, especially under nitrogen-deprived conditions. Purple Non-Sulfur Bacteria (e.g., Rhodopseudomonas palustris): These bacteria can switch between various metabolic modes and produce hydrogen under light and anaerobic conditions.

Microbial biomass conversion utilizes microorganisms to degrade organic substrates, such as agricultural residues, wastewater, or biomass, to produce hydrogen. This process can be categorized into:

Dark Fermentation: Anaerobic bacteria break down organic compounds to produce hydrogen, typically yielding up to 4 moles of hydrogen per mole of glucose.

Microbial Electrolysis Cells (MECs): These systems apply a small external voltage to stimulate microorganisms to produce hydrogen from organic matter, enhancing efficiency and enabling continuous hydrogen production.

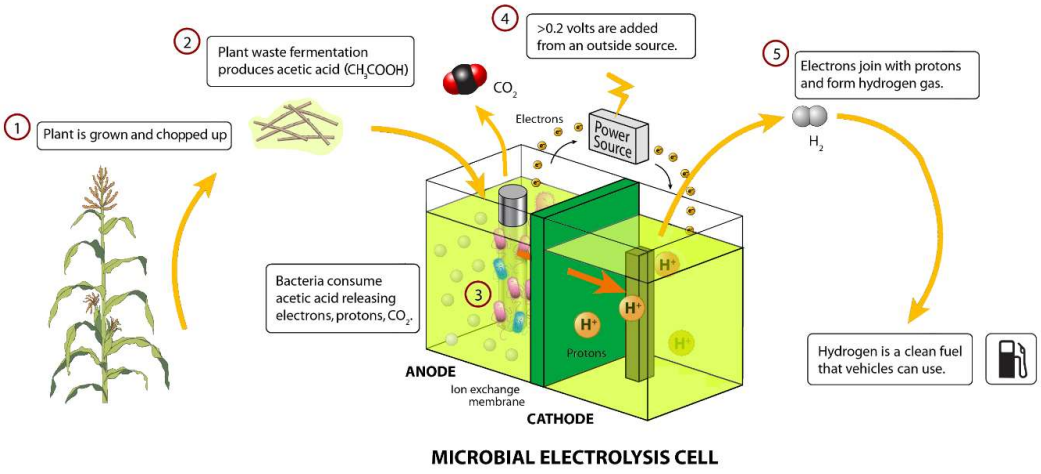


Figure 5: Microbial Electrolysis Cells [4]

Such processes are environmentally friendly and suitable for coupling with waste management systems, promoting circular economy practices.

1.3.2 The Future of Hydrogen

Government incentives, international climate agreements, and rising investments are accelerating the hydrogen economy. Countries across Europe, Asia, and North America are implementing national hydrogen strategies, focusing on low-carbon transportation, green industrial processes, and renewable-based power storage.

Hydrogen-Powered Transportation: Fuel Cell Electric Vehicles (FCEVs). FCEVs are gaining traction due to the benefits they offer compared to battery electric vehicles (BEVs)

Fast Refueling: Typically takes around 5 minutes.

Extended Range: Many FCEVs offer ranges exceeding 300 miles.

Energy Efficiency: Regenerative braking systems and energy-efficient drivetrains enhance overall performance.

In India, the Union Roads and Highways Authority has launched a pilot project for hydrogen-based advanced FCEVs, marking a significant shift towards environmental protection and reduced fossil fuel dependence.

Hydrogen Trains:

Hydrogen-powered trains are being developed as a cleaner alternative to diesel-powered locomotives. India's Initiative: Chhattisgarh has introduced India's first hydrogen-powered fuel cell truck, developed by Adani Enterprises in partnership with Indian and international technology firms. This initiative aims to reduce reliance on diesel and set a national standard for cleaner transportation.

Hydrogen Ships and Aircraft:

The maritime and aviation sectors are exploring hydrogen as a sustainable fuel. India's Plans: India aims to transition all coastal and inland waterway shipping to renewable energy sources within the next five years, supporting the goal of net-zero carbon emissions by 2070. The first Indian-made hydrogen-run ferry has been launched, and plans are in place to develop solar-powered and battery-operated green energy vessels.

India's Hydrogen Strategy:

India is positioning itself as a leader in the hydrogen economy through a combination of a national Plan to achieve an annual production capacity of 5 million metric tons of green hydrogen by 2030.Infrastructure Development: Establish green hydrogen hubs and develop necessary infrastructure for supply chains, including pipelines and refueling stations.

Several Indian states are actively developing hydrogen strategies:

Kerala: The Kerala Green Hydrogen Valley project aims to establish a fully integrated hydrogen ecosystem, including hydrogen-powered buses, trucks, and boats. The state offers subsidies for refueling stations and tax incentives for hydrogen production.

Andhra Pradesh: The state has inaugurated a ₹22,000 crore integrated clean energy project, with a focus on renewable energy and green hydrogen production.

West Bengal: The state has launched the Green Hydrogen Policy 2023, aiming for a 20% renewable energy share by 2030 and promoting investments in green hydrogen infrastructure

Global Collaborations and Investments

India is attracting significant investments in the green hydrogen sector: Juno Joule Green Energy and Select Energy, A joint venture to develop a green hydrogen and ammonia production facility in Andhra Pradesh, with an investment of approximately ₹10,000 crore.

BPCL and Sembcorp: A cooperative initiative to support green hydrogen and renewable energy projects across India, reflecting the country’s ambition to reach a clean energy capacity of 500 GW or above by 2030.

With appropriate policy, innovation, and infrastructure, hydrogen could play a crucial role in establishing a clean, resilient, and circular energy future.

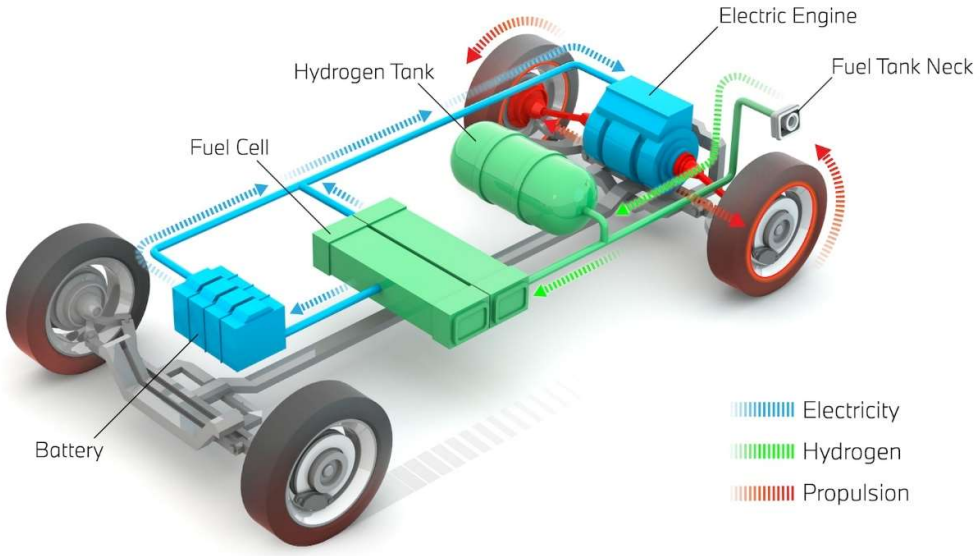


Figure 6: Hydrogen Fuel Cell Cars

(source: BMW.com)

1.4 Role of PEC Cells and Solar Integration

Photoelectrochemical (PEC) cells offer a promising and direct method for converting solar energy into hydrogen through water splitting. These systems use semiconductor photoelectrodes to absorb sunlight and generate charge carriers (electrons and holes) that drive the redox reactions needed to produce hydrogen and oxygen. The compact design of PEC cells integrates both light-harvesting and electrochemical functions, minimizing energy losses and reducing system complexity.

In the initial phase of this study, a PEC system was designed using a TiO_2 photoanode, paired with platinum cathodes and a proton exchange membrane (PEM). The TiO_2 material, known for its chemical robustness and stability, was effective in initiating water oxidation under UV light. A solar dish concentrator setup was employed to focus sunlight onto the PEC cell, enhancing irradiance and increasing the generated photocurrent and photovoltage. This configuration allowed the system to operate without any external power source, relying solely on focused solar energy to drive the hydrogen evolution reaction.

Building on the foundational results with TiO_2, the project progressed to incorporating InGaN/GaN nanowire-based photoanodes, aiming to overcome the limitations associated

with TiO_2's narrow absorption range. The InGaN/GaN nanostructures offer a tunable bandgap that extends light absorption well into the visible spectrum, significantly increasing solar utilization. Their nanowire morphology provides a high surface-to-volume ratio, enhancing charge separation and transport efficiency. When integrated with the same PEM-based PEC cell and solar concentrator setup, this advanced electrode material is expected to deliver improved photocurrent density and higher hydrogen production efficiency under concentrated sunlight.

This evolution from stable oxide-based systems to advanced III-nitride nanostructures demonstrates a practical pathway toward more efficient and scalable PEC technologies for off-grid, sustainable hydrogen production. Additionally, the potential use of wastewater as an electrolyte presents a dual benefit of energy generation and environmental remediation, further supporting the viability of PEC systems for decentralized clean energy solutions.By eliminating the need for grid power and utilizing only solar energy, PEC systems provide a decentralized solution for hydrogen production, making them particularly suitable for remote and off-grid locations. Moreover, by incorporating wastewater as an electrolyte medium, such systems can simultaneously address energy and environmental challenges.

1.5 Objectives of the Study

- To design and model a chemically stable and high-efficiency InGaN/GaN superlattice-based nanowire photoelectrode, which significantly enhances light absorption, charge carrier separation, and photocurrent output across the solar spectrum.
- To develop a solar-driven, self-bias PEC system that efficiently splits water into hydrogen and oxygen, eliminating the need for external grid power and enabling operation in off-grid or remote environments.
- To integrate solar concentrator technology into the PEC setup to amplify solar irradiance on the photoelectrode surface, thereby increasing photovoltage and overall PEC efficiency.
- To enable simultaneous treatment of industrial wastewater by leveraging MFC-based anode-respiring bacteria that degrade recalcitrant organic compounds, converting pollutants into less harmful by-products while generating additional current.

- To apply semiconductor bandgap engineering techniques to extend photoresponse deeper into the visible spectrum, maximizing the use of incident solar energy for improved photocatalytic performance.
- To evaluate theoretical and experimental hydrogen production rates, solar-to-hydrogen (STH) efficiency, and system performance under varying solar and wastewater conditions.
- To demonstrate a scalable design capable of handling large volumes of industrial effluents, ensuring practical applicability and societal benefit by turning waste into a resource.

1.6 Scope of the Work

The scope of this research encompasses the conceptual design, theoretical modeling, and performance evaluation of a lab-scale solar-driven photoelectrochemical (PEC) system for hydrogen production and wastewater treatment. The initial phase involved the modeling of a PEC system using TiO_2 as the photoanode, platinum as the cathode, and a proton exchange membrane (PEM) to facilitate proton transport and maintain compartmental separation.

Building upon this foundational work, the project progressed to incorporate InGaN/GaN nanowire-based photoelectrodes, aiming to enhance photocurrent density and broaden the absorption of solar energy into the visible spectrum through bandgap engineering and nanostructuring. The study also includes the design and analysis of solar concentrator geometries, optimizing the delivery of focused solar irradiance to the working electrode to increase photovoltage and drive self-sustained water splitting without external bias.

The research further involves evaluating the theoretical hydrogen production rate, solar-to-hydrogen (STH) efficiency, and overall system performance based on material properties and system configuration. While the work is currently limited to simulation, modeling, and analytical calculations, it lays the groundwork for future experimental validation, integration with microbial fuel cells (MFCs), and scaling up for industrial wastewater treatment and decentralized hydrogen generation systems.

1.7 Thesis Organization

Chapter 1: Introduction

Chapter 2: Review of related literature and existing PEC technologies

Chapter 3: System modeling, material specification, and design methodology

Chapter 4: Theoretical analysis and performance calculations

Chapter 5: Conclusions, implications, and future research directions

References: Comprehensive list of sources and supporting literature

2

LITERATURE REVIEW

2 Literature Review

2.1 PEC

Hydrogen is increasingly being recognized as a cornerstone of a clean energy future due to its zero-emission characteristics and flexibility in application. Among various production techniques, Photoelectrochemical (PEC) water splitting stands out as a direct and sustainable method for hydrogen generation using solar energy. This chapter reviews previous research in PEC systems, novel materials, and solar integration, emphasizing their relevance to the current study.

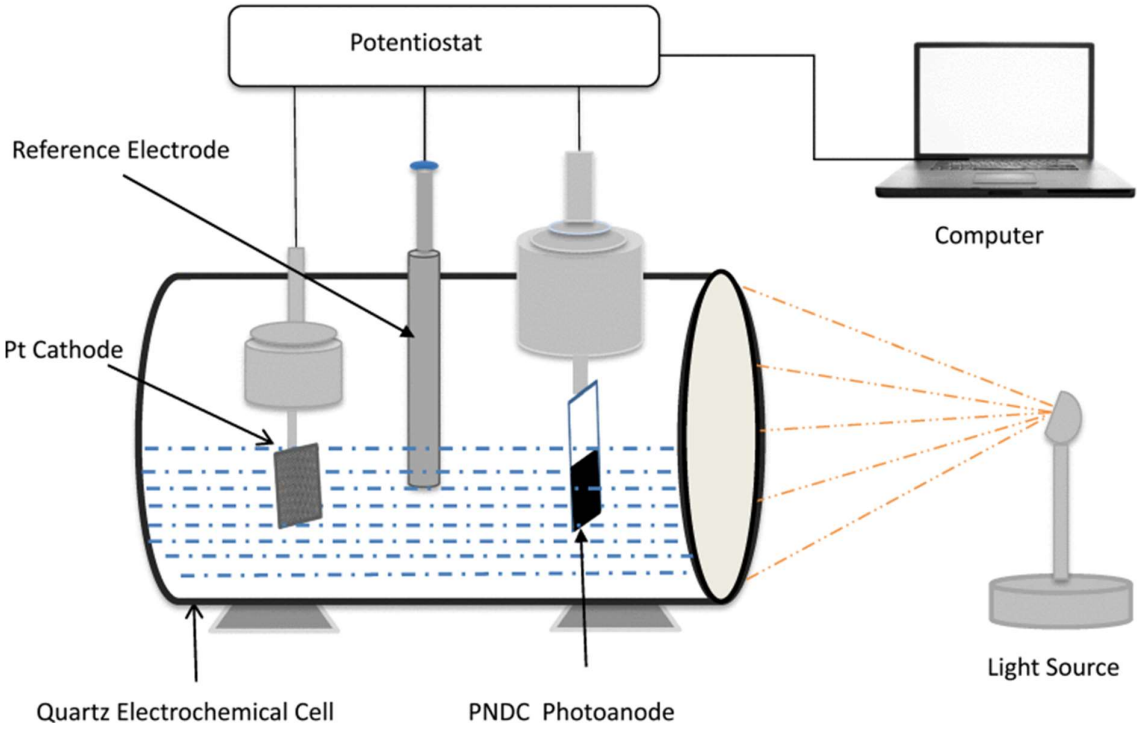


Figure 7: PEC Characterization Setup [2]

Hydrogen has emerged as a critical component in the global shift toward sustainable and decarbonized energy systems. Among various production techniques, photoelectrochemical (PEC) water splitting has attracted attention for its ability to generate hydrogen directly from solar energy using semiconducting materials. This chapter reviews the advancements in PEC-based hydrogen generation, material innovations, device

architectures, and modeling techniques relevant to the current study on a solar-driven, self-bias PEC system.

2.1.1 Overview of PEC Water Splitting

The photoelectrochemical (PEC) method uses sunlight to drive the separation of water into hydrogen and oxygen, presenting a viable way to create clean hydrogen fuel. The PEC cell comprises a photoanode and a cathode, immersed in an electrolyte, where solar photons generate electron–hole pairs to drive the water splitting reaction. The fundamental breakthrough was achieved by Fujishima and Honda (1972), who demonstrated water oxidation using TiO_2 under UV light. However, widespread use has been limited due to material challenges, efficiency bottlenecks, and stability issues under operating conditions.

2.1.2 Titanium Dioxide (TiO_2)-Based Systems

TiO_2 is the most extensively researched photoanode material because of its excellent chemical stability, plentiful availability, and non-toxic properties. However, its wide bandgap (~3.2 eV) limits its activity to UV light absorption, representing only ~4% of the solar spectrum. To overcome this, research has focused on: Doping with non-metallic elements (e.g., N, P, S), Surface modifications, and Composite structures with conductive materials like graphene. Graphene–TiO_2 composites have shown improved photocatalytic activity, with one study showing up to 41× greater hydrogen yield compared to pure TiO_2.

2.1.3 Carbon-Based Photocatalysts and Doping Strategies

Carbon-based materials like graphitic carbon nitride (g-C_3N_4) have become promising alternatives to metal oxides due to: Better visible-light absorption, Tailorable electronic properties, and Lower environmental impact.

Studies show: Pristine g-C_3N_4 has a bandgap of ~2.7 eV. Sulfur-doped g-C_3N_4 further reduces the bandgap, increasing hydrogen evolution to ~136μmol/h.A notable breakthrough by Sharma et al involved the use of Phosphorus–nitrogen-doped carbon (PNDC), which showed a photocurrent density of 0.416 mA/cm² under visible light, offering a new class of low-cost, metal-free photoanodes.

2.1.4 Composite Photoelectrodes and rGO-Based Counter Electrodes

Hybrid designs incorporating advanced materials like IGZO/TiO_2 composite films and reduced graphene oxide (rGO)-modified platinum electrodes have improved charge

transport and surface reactivity. Chou et al. showed a 28% increase in efficiency over pure TiO_2.

The addition of rGO increased short-circuit current and fill factor by enhancing interfacial conductivity and minimizing recombination losses. These composites represent a step forward in engineering multifunctional electrodes for DSSCs and PEC systems.

2.1.5 Proton Exchange Membranes (PEMs)

PEMs are crucial components in PEC and electrolyzer systems. They: Provide proton conductivity, Prevent gas crossover, Enable bias-free operation in some configurations. Nafion membranes are most commonly used due to their mechanical strength and ionic selectivity, and are featured in this thesis's PEC cell design.

2.1.6 III–V Semiconductor Materials

Group III–V semiconductors such as GaAs, InP, and InGaN have received attention due to their: Bandgap tunability, Favorable band-edge positions, High solar absorption.

Challenges include: High material cost, Corrosion in aqueous environments. Protective strategies such as atomic layer deposition (ALD) of TiO_2, incorporation of MoS_2 co-catalysts, and tandem architectures have been used to improve durability and efficiency.InP-based systems have reached STH efficiencies up to 11.6%, showcasing the potential of these materials when adequately protected.

Table 1: List of semiconductors and band gaps

Semiconductor	Band gap (eV)	Semiconductor	Band gap (eV)
Fe_2O_3	2.3	CdSe	1.7
CdS	2.5	g-C_3N_4	2.7
WO_3	2.8	Cu_2O	2.2
TiO_2 (rutile)	3.0	V_2O_5	2.4
TiO_2 (anatase)	3.2	CeO_2	2.94
ZnO	3.2	ZnS	3.6
SnO_2	3.5	SiC	3.0

2.1.7 Technoeconomic and System-Level Analysis

Technoeconomic studies, including those supported by the U.S. DOE, classify PEC systems into four types: Colloidal particle suspension systems, Immobilized particle bed systems, Photovoltaic-electrolyzer hybrid panels, Concentrated PEC panel systems. Type

4 (concentrated PEC systems) have shown promise in scalability and cost reduction, with hydrogen production costs projected under $3/kg if efficiencies above 10% and lifetimes beyond 5 years are achieved.

2.1.8 PEC Systems Using Wastewater as Electrolyte

Emerging research focuses on using wastewater as an electrolyte, offering: Cost-effective hydrogen production, Simultaneous wastewater treatment, and Integration with circular economy principles. This concept is central to the present thesis, which explores PEC systems capable of decentralized and sustainable hydrogen generation with additional environmental benefits.

2.2 Material Innovations in PEC Cells

Traditional PEC cells rely heavily on metal oxide semiconductors like TiO_2, WO_3, and Fe_2O_3 due to their chemical stability and abundance. However, these materials have large band gaps, limiting their absorption to UV radiation.

To overcome this, recent innovations have explored heteroatom doping and carbon-based photocatalysts: Sharma et al. (2016) developed a phosphorus–nitrogen-doped carbon (PNDC) material, which achieved a photocurrent density of 0.416 mA/cm² under visible light. This novel material combines high surface area, visible-light activity, and stability, addressing multiple limitations of traditional photocatalysts.

Graphitic carbon nitride (g-C_3N_4) and its doped variants (e.g., S-doped) showed enhanced H_2 production rates (up to 136 μmol/h), providing new pathways for developing low-cost, non-metallic photoelectrodes.

2.3 Composite Films and Nanostructures

The integration of materials like indium gallium zinc oxide (IGZO) with TiO_2 has improved photoelectrode efficiency: Chou et al. (2018) demonstrated a composite IGZO/TiO_2 photoelectrode paired with a reduced graphene oxide/platinum (rGO/Pt) counter electrode, which boosted DSSC efficiency by 28%. The IGZO provided uniform porosity and higher electron mobility, reducing recombination and enhancing charge transfer.

In efforts to enhance the performance of photoelectrochemical (PEC) and dye-sensitized solar cell (DSSC)-based hydrogen production systems, researchers have explored

advanced composite structures and nanomaterials that improve charge transfer, surface reactivity, and light absorption.

A notable development is the use of IGZO/TiO_2 composite photoelectrodes paired with reduced graphene oxide/platinum (rGO/Pt) counter electrodes. These hybrid materials are engineered to optimize both the electrochemical and morphological properties of PEC systems.

Chou et al. (2018) fabricated a composite photoelectrode by depositing Indium Gallium Zinc Oxide (IGZO) on a double-layered TiO_2 structure using RF sputtering. This composite improved the surface morphology and porosity of the photoelectrode, which enhanced light absorption and increased the reactive surface area. The IGZO addition increased electron mobility (>10 $cm^2/V \cdot s$), improving electron diffusion across the TiO_2 layer. The average thickness of the IGZO/TiO_2 layer was ~16.7 μm, with the absorption layer held constant at 6.3 μm.

Table 2: DSSC Photovoltaic Properties Based on Different Counter and Photoelectrode Combinations

Counter electrode (CE)	Photoelectrode (PE)	V_{OC} (V)	J_{SC} (mA/cm^2)	F. F. (%)	η (%)	V_{MAX} (V)	I_{MAX} (mA)
Pt	TiO_2	0.63	6.74	62.09	2.64	0.45	0.91
Pt	IGZO/TiO_2	0.65	8.33	63.32	3.38	0.49	1.08
rGO/Pt	IGZO/TiO_2	0.66	9.39	62.25	3.88	0.47	1.32
Pt	Sn/TiO_2	0.70	4.96	64.30	2.25 [36]	NA	NA
Pt	Zno	0.74	4.23	74.00	2.23 [37]	NA	NA

Reduced Graphene Oxide (rGO)/Platinum Counter Electrode: To complement the composite photoanode, rGO was deposited onto a platinum counter electrode to boost electrical conductivity and expand the electrochemically active surface area. The rGO/Pt counter electrode was fabricated through spin coating using a solution composed of rGO, TiO_2 nanoparticles, and surfactants. This configuration enhanced the short-circuit current density (JSC) and overall photoelectrochemical (PEC) efficiency (η) by improving electron diffusion and transfer at the counter electrode interface.

Photovoltaic Performance: The DSSC incorporating both innovations showed an increase in efficiency by 28% and JSC by 24% when comparing IGZO/TiO_2 to traditional TiO_2.An additional 14% boost in efficiency with rGO/Pt counter electrodes,

Open-circuit voltage (VOC): 0.66 V

Short-circuit current density (JSC): 9.39 mA/cm²

Fill factor (FF): 62.25%

Efficiency (η): 3.88%

These enhancements were attributed to: IGZO's superior field-effect mobility, reduced recombination due to better surface uniformity, and increased interfacial conductivity from rGO, which supports faster charge transfer and suppresses electron loss.

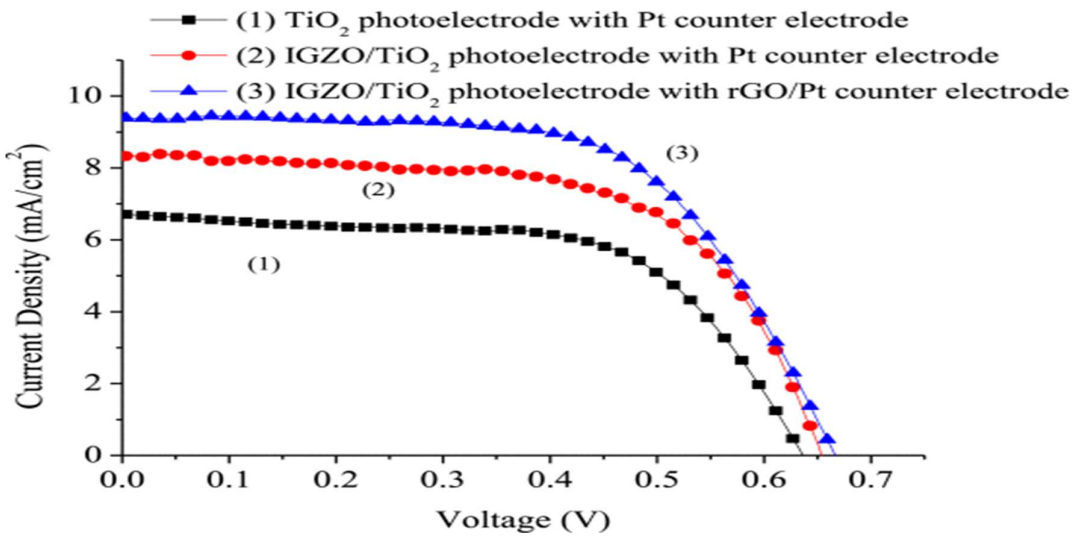


Figure 8: J–V curves of DSSCs with different counter electrodes and photoelectrodes [6]

2.4 Role of Proton Exchange Membranes (PEM)

Proton Exchange Membranes are critical for maintaining ionic conductivity and preventing gas crossover in PEC systems. Nafion-type PEMs, as used in fuel cells and PECs, ensure the separation of the oxygen and hydrogen evolution reactions while minimizing ohmic losses. Studies have shown that PEM-integrated PEC designs are more robust and maintain stable operation in real-world conditions. As hydrogen energy systems expand into sophisticated electrical applications, accurate modeling and simulation become essential for designing efficient and reliable systems. One area of growing research interest is the integration of PEM fuel cells (PEMFCs) with superconducting devices (SCs), enabled by dynamic system modeling in environments such as MATLAB/Simulink.

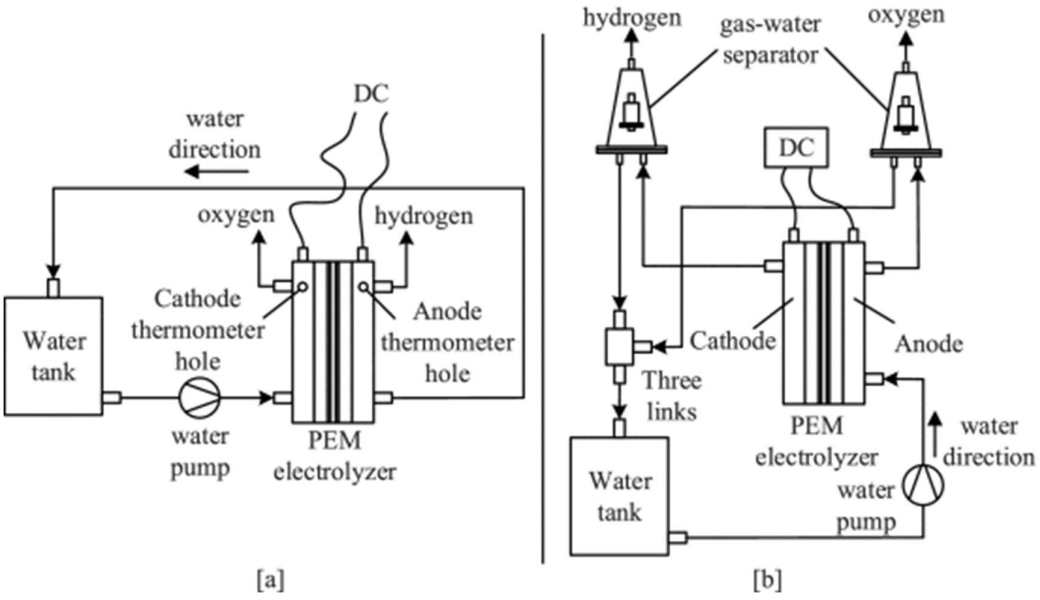


Figure 9: PEM set up [13]

2.5 PEMFC Modeling Framework

The behavior of PEMFCs can be mathematically modeled through a set of equations derived from electrochemical processes, including: Faradaic reactions at the anode and cathode, Mass and charge transfer phenomena, Electrochemical potential losses such as activation, ohmic, and concentration losses. In a typical MATLAB/Simulink model:

The PEMFC is simulated as a dynamic current source. The hydrogen flow rate governs output current control. A 1D electrical equivalent model (based on voltage-current characteristics) replicates real-world PEMFC behavior without modeling channel-level gas dynamics.

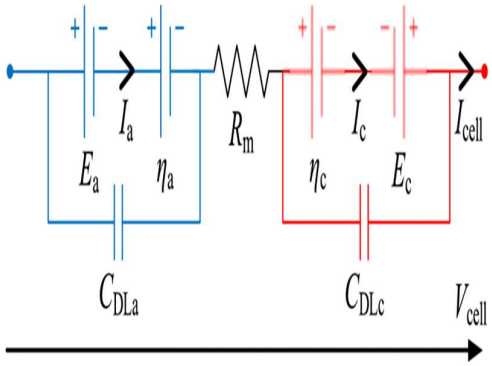


Figure 10: Electric dynamic model of a single PEM fuel cell [13]

These inputs allow reproduction of PEMFC voltage (Vcell) through the following combined equation: This equation models the net cell voltage after accounting for cathodic and anodic overpotentials (η), membrane resistance (η_m), and internal activation losses.

2.5.1 Superconducting Coil (SC) Model

The superconducting coil in these simulation studies is modeled as a perfect inductance (L) in series with a low-value resistance (R) that simulates the resistance of the connecting wire. For example, A 4 mH coil was connected via a 4 mΩ wire in experimental validation.

Further simulations explored inductances from 1 H to 10 H with varying resistive connections. This RL configuration models the transient and steady-state behavior of the SC when supplied by a PEMFC under different hydrogen flow rates and wire lengths.

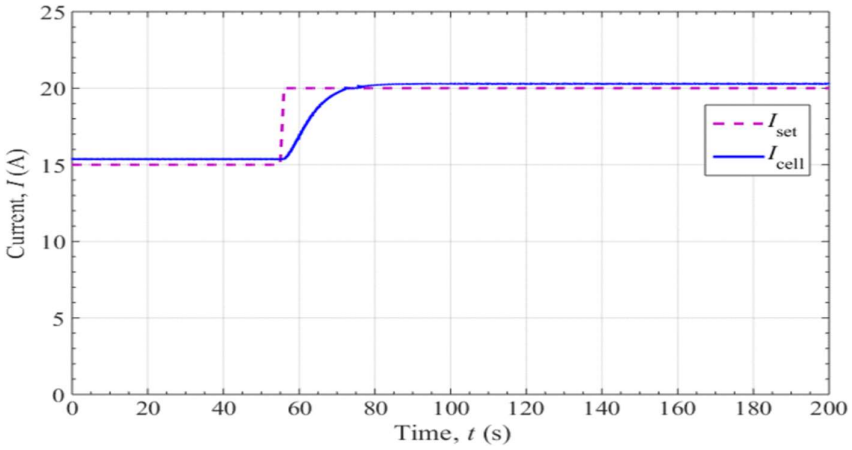


Figure 11The simulated current (I_cell) of a PEMFC connected through a 4 mΩ wire to a 4 mH superconducting coil, illustrating the response when I_set changes abruptly from 15 A to 20 A. [12]

2.5.2 System-Level Integration and Validation

The MATLAB Simulink model integrates both components: The PEMFC operates as a current-controlled source driven by hydrogen flow. The SC is modeled as a perfect inductance L_SC in series with a resistance R_wire.

Simulations validate the design by reproducing current behavior and voltage drops consistent with experimental measurements from a system using: A PEMFC with 100 cm² active area, a 4 mH SC load, and A 4 mΩ connection wire.

Model outputs were compared with lab-based measurements to confirm accuracy. Simulation sweeps across a range of inductance values (1–10 H) and wire resistances were conducted to determine design limits, particularly the maximum permissible distance between the PEMFC and SC.

2.6 Solar Concentrators and Self-Biasing

Efficiency in PEC systems is limited by the inherent energy conversion potential of semiconductors. To address this, solar concentrators (like parabolic dishes) have been integrated to:

- Increase irradiance
- Enhance photocurrent density
- Enable self-biasing operation without external power sources

Ardo et al. (2018) and DOE-funded studies demonstrated that solar-concentrated PEC systems can deliver better cost-to-output ratios and are viable for off-grid hydrogen production.

2.7 Hybrid Applications and Integration

An emerging trend in PEC research is hybridizing energy generation with wastewater treatment, thus combining environmental remediation with fuel production.

PNDC electrodes, owing to their catalytic nature and stability, are promising candidates for such dual-function systems.

Fuel cell integration with PEC or electrolyzer systems offers a modular design capable of energy storage, power generation, and grid independence.

2.8 Challenges Identified in Literature

- Despite progress, several bottlenecks persist:
- Material stability under continuous solar exposure
- Low STH efficiencies, typically <5% for most reported PEC systems
- High production costs, particularly for platinum-based cathodes
- Scalability issues, due to fragile semiconductor interfaces and corrosion

3

DESIGN METHODOLOGY

3 DESIGN METHODOLOGY

3.1 Overview

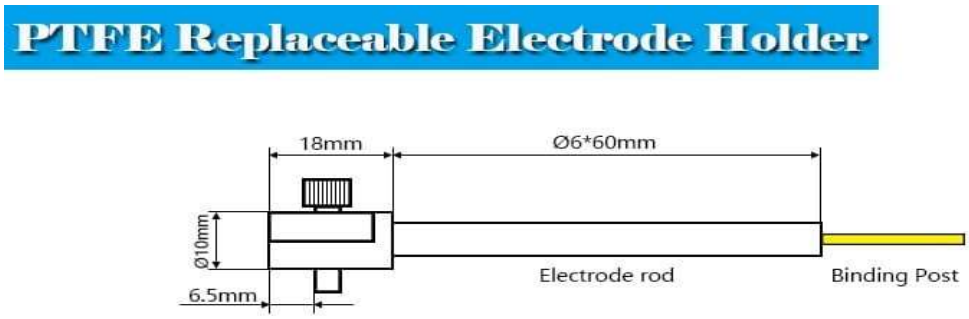
The photoelectrochemical (PEC) cell developed in this study harnesses solar energy to drive water splitting into hydrogen and oxygen without the need for an external electrical bias. The cell comprises a working electrode, a counter electrode, a reference electrode, a proton exchange membrane, and a customized electrolyte solution. The system operates under focused solar illumination to enhance reaction efficiency and achieve self-biasing.

3.2 Material specification

3.2.1 Working Electrode

When sunlight hits the working electrode, usually coated with a semiconductor such as TiO_2, the photon energy is absorbed, causing electrons to be excited from the valence band to the conduction band of the semiconductor. This process generates electron–hole pairs, negatively charged electrons, and positively charged holes. The holes then move to the electrode surface, where they facilitate the oxidation of water molecules, producing oxygen and protons. Meanwhile, the excited electrons travel through the electrode and external circuit toward the cathode, enabling the reduction of protons to hydrogen gas. This flow of electrons, driven by sunlight, constitutes the photoelectric effect fundamental to the PEC cell's operation.

Figure 12a): working electrode. (source: DEK RESEARCH INSTRUMENTATION)



Detailed parameter table						
Name	Conductive Material	Sheetmetal Size (mm)	Thickness of clampable sample	Rod Material	Rod Size (mm)	Binding Post
WE	Platinum, Gold, Titanium, Copper,etc	10*15mm	0~5mm	PTFE	Ø6*60 (can be customized)	Gold-plated copper rod
Note: PTFE replaceable electrode holder size can be customized						

Figure 13b): Detailed parameter table of the electrode holder. (source: DEK RESEARCH INSTRUMENTATION)

When exposed to sunlight, photons with energy equal to or exceeding the bandgap of the semiconductor (such as TiO_2) on the working electrode are absorbed, causing electrons to be excited from the valence band (VB) to the conduction band (CB). This photon absorption results in the generation of electron–hole pairs (e^-/h^+). The photogenerated holes (h^+) migrate to the semiconductor–electrolyte interface, where they drive the oxidation of water molecules ($H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$). Concurrently, the electrons (e^-) are transported through the semiconductor and the underlying titanium substrate to the external circuit. This charge separation and directional electron flow minimize recombination losses, enabling the electrons to reach the counter electrode where they reduce protons (H^+) to hydrogen gas ($2H^+ + 2e^- \rightarrow H_2$). The efficiency of this process depends critically on the semiconductor's band structure, charge carrier mobility, surface states, and interface kinetics.

Working Electrode: Photon-Induced Charge Generation and Water Oxidation

When the working electrode coated with a semiconductor (e.g., TiO_2) is illuminated by sunlight, photons with energy

$h\nu \geq Eg$ (where Eg is the semiconductor bandgap) are absorbed. The process excites electrons from the valence band (VB) into the conduction band (CB), leading to the formation of electron–hole pairs: Semiconductor

$+h\nu \rightarrow e\mathrm{CB} - + h\mathrm{V}$

The photogenerated holes move to the electrode surface, where they drive the water oxidation reaction:

$2H_2O \rightarrow O_2 + 4H + + 4e^-$

This can be summarized at the photoanode as:

$4h + + 2H_2O \rightarrow O_2 + 4H$

Simultaneously, the excited electrons flow through the semiconductor and titanium substrate into the external circuit, minimizing electron–hole recombination. These electrons travel to the counter electrode, where they reduce protons:

$4\mathrm{H} + + 4\mathrm{e}^- \rightarrow 2\mathrm{H}\ 2$

This directional charge separation drives the overall water splitting reaction:

The efficiency of charge separation and transport at the working electrode is critical for sustaining continuous water oxidation and hydrogen production without external bias.

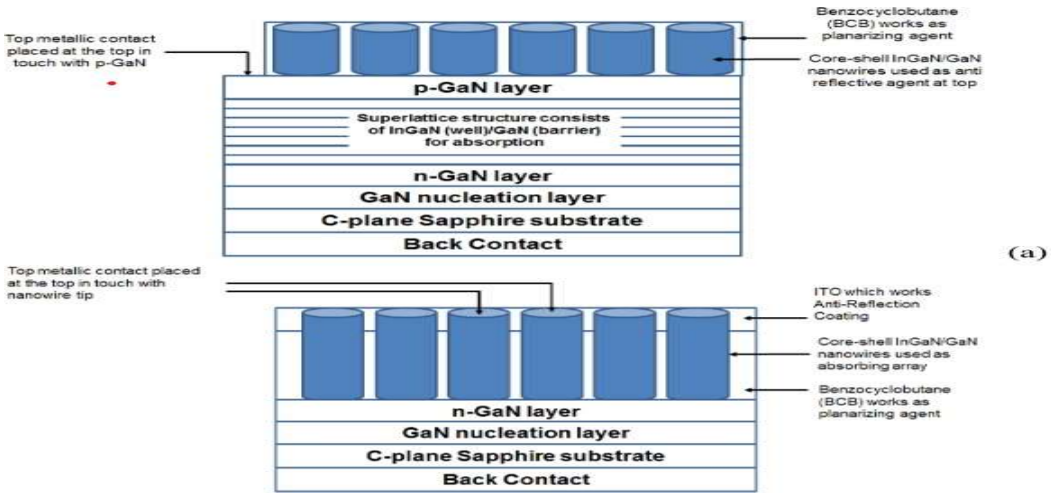

Top metallic contact placed at the top in touch with p-GaN
Benzocyclobutane (BCB) works as planarizing agent
Core-shell InGaN/GaN nanowires used as anti reflective agent at top
p-GaN layer
Superlattice structure consists of InGaN (well)/GaN (barrier) for absorption
n-GaN layer
GaN nucleation layer
C-plane Sapphire substrate
Back Contact
(a)
Top metallic contact placed at the top in touch with nanowire tip
ITO which works Anti-Reflection Coating
Core-shell InGaN/GaN nanowires used as absorbing array
Benzocyclobutane (BCB) works as planarizing agent
n-GaN layer
GaN nucleation layer
C-plane Sapphire substrate
Back Contact

Figure 14: working electrode using group III nitrides (InGaN/GaN)

When exposed to incident radiation (light), the photoelectrode absorbs photons causing the formation of electron-hole pairs in the InGaN material due to its light-absorbing properties.

$h\nu \geq Eg \Rightarrow$ Photon absorbed

The photogenerated electrons are transported through the InGaN/GaN nanowire to the external circuit. The holes are transferred to the solution (electrolyte) at the surface of the photoelectrode, facilitating the oxidation reaction. Electrons returning from the external circuit reduce protons (H^+) from the solution into hydrogen gas (H2). This reaction occurs at the counterelectrode. The reference electrode (e.g., Ag/AgCl) is used to measure the potential of the working electrode accurately without influencing the reaction.

$InGaN+h\nu \rightarrow e\ CB^{-}+hVB+$

The InGaN/GaN nanowire photoelectrode is designed to absorb sunlight efficiently.InGaN is a direct bandgap material whose bandgap can be tuned by adjusting the indium composition, making it ideal for harvesting photons from visible to near-ultraviolet regions. Sunlight (containing photons with energy hν) is directed onto the photoelectrode. Photons with energy (hν) higher than the bandgap energy (Eg) of InGaN are absorbed, resulting in electron-hole pair generation. Photon Absorption: The InGaN nanowire array absorbs incoming photons from sunlight. The high surface area of nanowires enhances the probability of photon absorption.

Charge Generation: The absorbed photons excite electrons from the valence band to the conduction band, leaving behind holes in the valence band.

Charge Carrier Separation: Electrons move through the conduction band of the nanowire to the n-GaN layer and then to the back contact. Holes

migrate toward the surface of the nanowires for participation in oxidation reactions.

$2Br^{-} \rightarrow Br_2+2e^{-}$

Catalytic Reactions: At the surface of the photoelectrode, holes facilitate the oxidation of the electrolyte, releasing bromine gas (Br_2) and generating protons (H^+).

At the electrode–electrolyte interface, the photogenerated holes oxidize water or halide ions, depending on the electrolyte composition. In the case of an HBr-based electrolyte, the oxidation reaction at the photoanode surface leads to the generation of bromine gas and protons. Water-based PEC operation:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

These reactions contribute to the accumulation of protons in the anodic chamber, which then diffuse through the proton exchange membrane (PEM) to the cathodic side. The electrons that left the photoanode travel via the external circuit to the counter electrode, where they participate in hydrogen evolution.

The charge separation and transport efficiency in the photoanode are critical for minimizing recombination losses and enhancing overall PEC performance. The nanowire geometry significantly improves light trapping and charge transport by increasing the effective surface area and providing direct pathways for charge carriers. Additionally, the GaN shell encapsulating the InGaN core provides robust protection against photocorrosion, ensuring long-term material stability in harsh electrolyte environments.

In essence, the photoanode serves as the primary energy conversion interface, absorbing incident solar photons and driving the oxidation half-reaction. The efficient generation, separation, and transport of photogenerated carriers at the working electrode directly govern the rate of hydrogen production and the sustainability of the PEC process.

3.2.2 Counter Electrode

Material: Platinum sheet. The counter electrode in a photoelectrochemical (PEC) cell serves as the cathode where the reduction half-reaction occurs, primarily facilitating the hydrogen evolution reaction (HER). For this study, a high-purity platinum (Pt) sheet was selected as the counter electrode due to its superior catalytic activity, excellent electrical conductivity, and exceptional corrosion resistance in acidic environments. The electrode was custom-fabricated to fit securely into the PEC cell assembly, ensuring optimal electrochemical contact and gas evolution efficiency.

The platinum sheet used for the counter electrode had dimensions of (10mm × 15mm × 0.1mm), providing a sufficient active surface area to support fast electron transfer and hydrogen generation without introducing mass transport limitations. The Pt sheet was

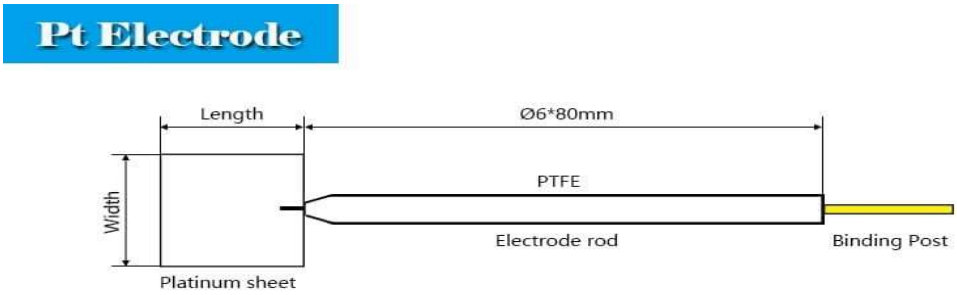
mounted on a PTFE (Polytetrafluoroethylene) rod using a replaceable clamping mechanism. This setup ensured both chemical inertness and mechanical rigidity. Electrical connection to the external circuit was achieved through a gold-plated copper binding post, minimizing contact resistance and preventing corrosion at the junction.

Design: PTFE-insulated rod integrated with the platinum surface.

Figure 15a): counter electrode (source: DEK RESEARCH INSTRUMENTATION)

The larger surface area of the platinum sheet electrode makes it compatible with sizable, sheet-shaped platinum working electrodes.

In a photoelectrochemical (PEC) cell, the counter electrode (CE) is an essential element responsible for facilitating the cathodic reaction, primarily the hydrogen evolution reaction (HER). In the present design, a high-purity platinum (Pt) sheet is employed due to its exceptional catalytic activity, excellent electrical conductivity, and long-term chemical stability in acidic environments. The counter electrode is securely mounted on a PTFE-insulated holder with a gold-plated binding post to ensure low-resistance electrical contact and corrosion protection.



Detailed parameter table					
Name	Sheet Material	Rod Material	Length*Width*Thickness (mm)	Rod Size (mm)	Binding Post
CE	Platinum (PT)	PTFE	10*10*0.1	Ø6*80 (can be customized)	Gold-plated copper rod
			10*10*0.2		
			15*15*0.1		
			15*15*0.2		
			20*20*0.1		
			20*20*0.2		
Note: Platinum sheet size can be customized					

Figure 16:b. Detailed parameter table of the counter electrode. (source: DEK RESEARCH INSTRUMENTATION*)*

During the operation of the photoelectrochemical (PEC) cell, sunlight illuminates the photoanode, producing electron–hole pairs. The photogenerated holes drive the oxidation of water at the photoanode surface, releasing protons (H^+) into the electrolyte. These protons then migrate through the proton exchange membrane (PEM) to the cathode chamber, where the counter electrode is located. At the same time, the photogenerated electrons are transported through the external circuit to the counter electrode, where they reduce the protons to generate molecular hydrogen gas (H_2).

The cathodic half-cell reaction taking place at the platinum surface can be expressed as:

$2H^+ + 2e^- \rightarrow H_2(g)$

Represents a hydrogen atom adsorbed onto the platinum surface. Platinum exhibits near-optimal hydrogen binding energy, which facilitates both adsorption and desorption steps, resulting in high exchange current densities and low overpotentials for HER.

In the context of a self-bias PEC system, the counter electrode does not require any external voltage to initiate the cathodic reaction. The built-in potential difference between the illuminated photoanode and the cathode is sufficient to drive the flow of electrons and sustain the redox processes. Therefore, the counter electrode is essential for maintaining

charge balance by receiving electrons from the external circuit and catalyzing the reduction of protons.

The hydrogen gas generated at the cathode is evolved as bubbles and collected separately from the oxygen produced at the anode. The design of the PEC cell ensures physical separation of the electrodes via the PEM, preventing gas crossover and recombination. Additionally, the platinum surface remains highly stable and active under prolonged operation, making it ideal for efficient and continuous hydrogen production.

In summary, the counter electrode facilitates the reduction half-reaction in the PEC cell and is integral to the operation of the self-sustained system. Its material properties, catalytic behavior, and electrochemical stability directly influence the efficiency and reliability of solar-driven hydrogen generation.

3.2.3 Reference Electrode

Construction: Microporous ceramic filter core filled with 3M/3.5M KCl solution.

The reference electrode serves as a stable potential reference point in the photoelectrochemical (PEC) cell, enabling accurate measurement of the working electrode's potential during operation. This study employs a silver/silver chloride (Ag/AgCl) reference electrode, which is made by coating high-purity silver wire with silver chloride and submerging it in a saturated KCl solution. This internal electrolyte is enclosed in a precision glass tubing sealed with a porous glass frit, which allows ionic contact with the external electrolyte while minimizing potential drift and contamination.

The electrochemical reaction governing the reference electrode is given by:

$$AgCl(s)+e^{-}\leftrightarrow Ag(s)+Cl^{-}(aq)$$

This redox equilibrium provides a stable potential, It commonly exhibits a potential of +0.197 V relative to the Standard Hydrogen Electrode (SHE) at 25°C when saturated KCl is used. The stability of this potential makes Ag/AgCl electrodes particularly suitable for aqueous PEC systems.

The reference electrode is positioned close to the working electrode within the anodic compartment of the PEC cell. It is typically inserted through a side port or held adjacent to the photoanode surface using a non-reactive holder. This placement ensures minimal

solution resistance and accurate potential measurement without interfering with the photochemical or electrochemical processes occurring at the photoanode.

The electrode body is fabricated from chemically inert borosilicate glass and sealed with a Teflon (PTFE) cap. Electrical connection is established via a gold-plated copper binding post, which ensures reliable signal transmission while preventing corrosion or potential distortion.

In a three-electrode photoelectrochemical (PEC) cell setup, the reference electrode plays a vital role in accurately and reliably measuring the electrochemical potential of the working electrode (WE). In this configuration, a silver/silver chloride (Ag/AgCl) electrode is utilized as the reference. Unlike the working or counter electrodes, the reference electrode remains electrochemically inert, meaning it does not engage in charge transfer or participate in redox reactions. Instead, it serves as a non-polarizable electrode that maintains a constant potential during PEC operation.

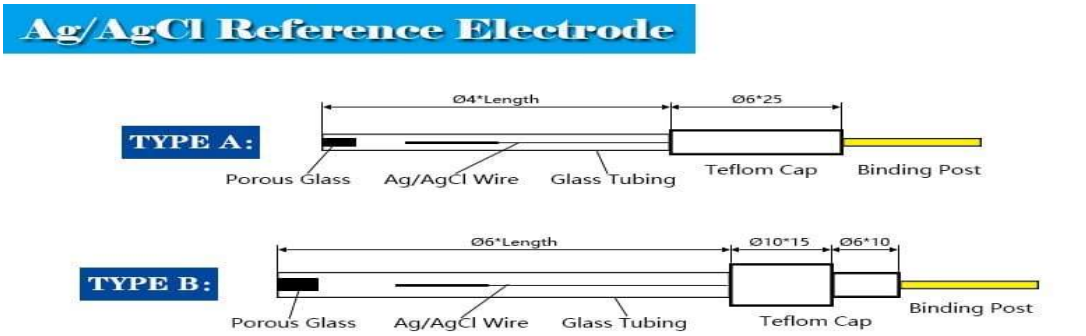
This equilibrium potential remains stable so long as the chloride ion concentration in the internal filling solution (usually saturated KCl) is constant. The typical standard potential for this electrode is:

During PEC operation, as the photoanode (working electrode) absorbs photons and generates electron–hole pairs, the reference electrode allows the potentiostat to continuously monitor the actual Potential difference between the working electrode and a fixed standard. This is essential for determining key parameters such as onset potential, photocurrent response, and overpotential for water oxidation or halide oxidation reactions.

Importantly, the reference electrode does not collect or supply electrons—it is positioned near the photoanode in the anodic compartment, typically close to the reaction interface, to minimize solution resistance and iR drop. Its design, consisting of a porous glass frit and inert body material like borosilicate glass with a Teflon sealing cap, ensures chemical inertness and electrical isolation.

In essence, the reference electrode acts as a stationary voltage probe, ensuring that the electrochemical behavior of the working electrode under solar illumination can be measured reproducibly, without introducing any significant current or chemical interaction into the PEC cell system.

Figure 17a): Reference electrode (source: DEK RESEARCH INSTRUMENTATION)



Detailed parameter table					
Type	Glass Tubing Size (mm)	Teflom Cap Size (mm)	Filling Solution	Applicable System	Binding Post
A	Ø4*50	Ø6*25	Saturated KCl solution	Neutral solution	Gold-plated copper rod
	Ø4*90				
B	Ø6*70	Ø10*15+Ø6*10			
	Ø6*140				
Note: Reference electrode size can be customized					

Figure 18: The detailed parameter table of the reference electrode (source: DEK RESEARCH INSTRUMENTATION)

Temperature Range: Operable between 0–100°C.

Function: Provides a stable reference voltage to measure electrode potentials accurately.

3.2.4 Proton Exchange Membrane (PEM)

The proton exchange membrane (PEM) plays a pivotal role in the operation of the photoelectrochemical (PEC) cell by facilitating selective proton transport while maintaining compartmental separation between the anodic and cathodic chambers. In this

study, Nafion™ N212 membrane is utilized due to its high proton conductivity, mechanical durability, and excellent chemical resistance under acidic and high-temperature conditions.

Nafion N212 is a perfluorosulfonic acid-based polymer with a hydrophobic PTFE backbone and hydrophilic sulfonic acid ($-SO_3H$) functional groups. These acidic groups form interconnected channels upon hydration, enabling fast and efficient proton (H^+) transport across the membrane. The essential physical properties of the membrane are its thickness of 51 μm, an area of 100 mm × 100 mm, and a proton conductivity of approximately 0.1 S/cm under hydrated conditions.

During PEC operation, water oxidation at the photoanode generates protons (H^+) and oxygen (O_2). The PEM selectively allows the passage of these protons from the anode chamber to the cathode chamber, where they participate in the hydrogen evolution reaction (HER). Meanwhile, the membrane effectively blocks gas crossover, especially of evolved O_2 and H_2, thereby preserving product purity and preventing explosive recombination reactions.

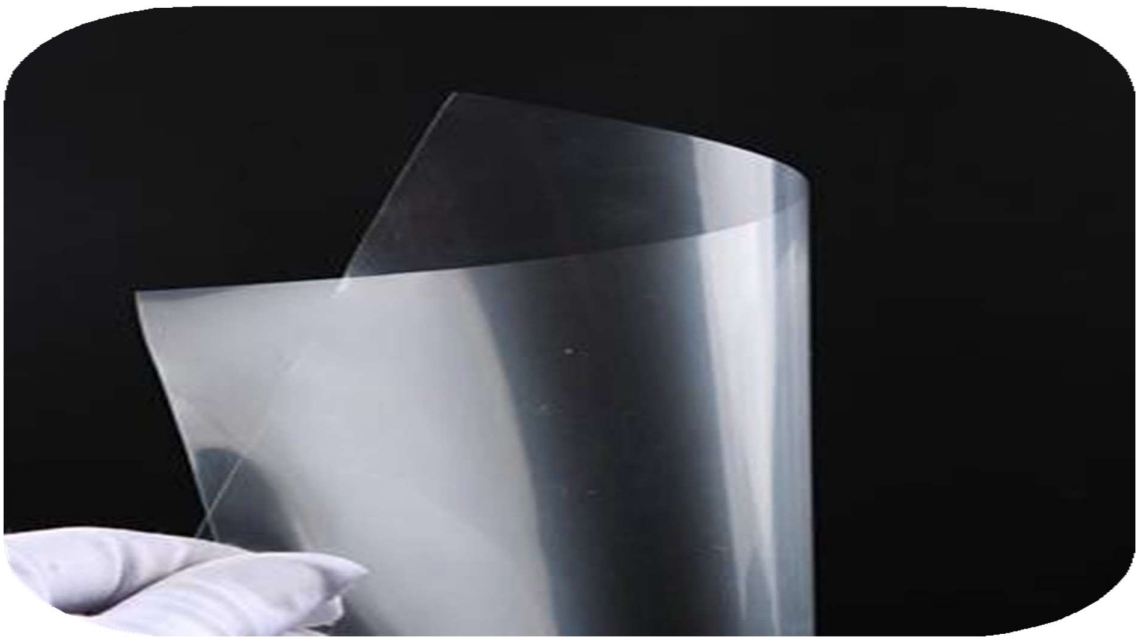


Figure 19a): PEM

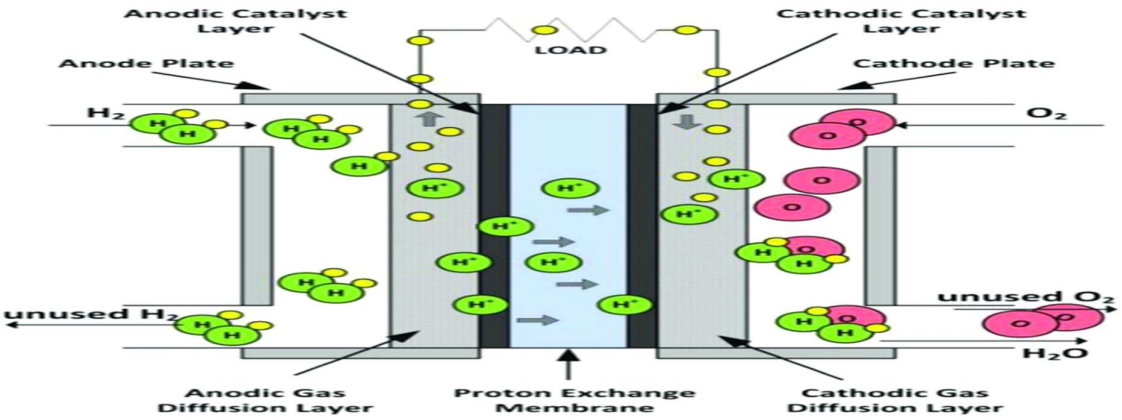


Figure 20b): Migration of H^+ ions from the anode to the cathode via the proton exchange membrane (PEM) [7].

The proton migration process can be represented as:

$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$(at the photoanode)

$2H^+ + 2e^- \rightarrow H_2(g)$(at the cathode)

By enabling ionic conductivity and suppressing unwanted mass transport, the PEM ensures charge neutrality, system efficiency, and long-term operational stability. The membrane also supports the self-bias configuration by minimizing internal resistance, thus maintaining effective coupling between the photovoltage of the working electrode and the redox kinetics at both electrodes. Proton conductivity as high as 0.1 S/cm, combined with low hydrogen crossover, and strong mechanical stability.

Function: Allows selective passage of protons (H^+) while preventing back-diffusion of gases like O_2 or Br_2.

3.2.5 Electrolyte Solution

Composition: 20 mL HBr + 100 mL distilled water.

An electrolyte solution containing 20 mL of hydrobromic acid (HBr) and 100 mL of deionized water (H_2O) provides an effective environment for the hydrogen evolution reaction (HER) in electrochemical cells.

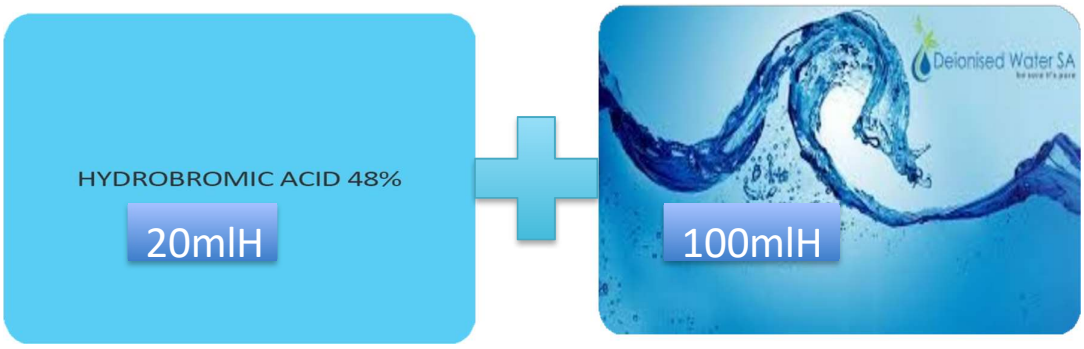


Figure 21: Electrolyte solution.

Upon dissolution, HBr dissociates into hydrogen ions (H^+) and bromide ions (Br^-), thereby providing a source of protons essential for the HER. The water component facilitates the conduction of these ions and supports the overall ionic conductivity of the electrolyte. This composition ensures efficient ion conduction, which is crucial for maintaining the electrochemical performance of the system.

In the context of the HER, the presence of H^+ ions allows for the reduction reaction at the cathode:

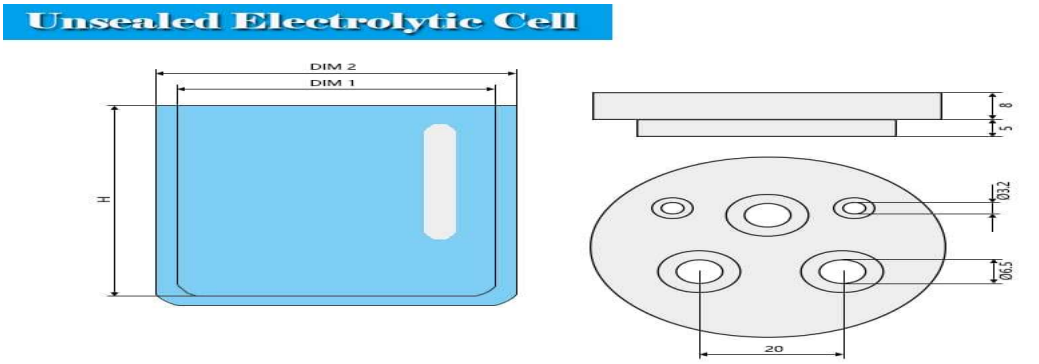
$$2H^+ + 2e^- \rightarrow H_2$$

This reaction leads to the evolution of hydrogen gas, a key process in water splitting and hydrogen production technologies. The electrolyte's composition and concentration are optimized to balance conductivity and proton availability, thereby enhancing the efficiency of the HER.

3.2.6 Quartz Tube

The incorporation of a quartz tube in the photoelectrochemical (PEC) setup contributes significantly to stability, efficiency, and optical performance of the system. Quartz is highly valued for its exceptional transparency across the ultraviolet (UV), visible, and near-infrared (NIR) spectrum, making it an ideal material for optical applications involving light-sensitive electrodes. In a PEC cell, the use of a quartz tube allows for maximum transmission of incident solar radiation onto the photoanode, thereby enhancing the photogeneration of charge carriers.

Figure 22a): quartz tube (source: DEK RESEARCH INSTRUMENTATION)



Detailed parameter table						
Volume (ml)	DIM1 (mm)	DIM2 (mm)	H (mm)	Hole Quantity	Electrode Hole Size (mm)	Vent Hole Size (mm)
150	55	60	70	3 electrode hole+2 vent hole (can be customized)	Ø6.5 (can be customized)	Ø3.2 (can be customized)
200	65	70	70			
Note: Hole size and position can be customized						

Figure 23: Detailed parameters of the Quartz tube (source: DEK RESEARCH INSTRUMENTATION*)*

Unlike conventional glass, quartz does not significantly absorb UV or high-energy visible light, which are essential components of the solar spectrum for driving photoelectrochemical reactions. Additionally, quartz exhibits excellent thermal and chemical resistance, which is vital for maintaining structural integrity during prolonged illumination and in the presence of highly acidic or corrosive electrolytes such as

hydrobromic acid (HBr). Quartz's mechanical robustness and chemical inertness also guarantee that the cell remains leak-tight and maintains optical stability under different experimental conditions.

From a structural perspective, the quartz tube serves as the main housing unit that securely holds the electrolyte and electrodes in place, while also accommodating inlet and outlet ports for gas evolution and electrolyte circulation. It provides a rigid, transparent framework that simplifies alignment with the solar simulator and allows for easy observation of bubble formation and gas evolution during the hydrogen generation process. The smooth, non-reactive inner surface of the quartz minimizes contamination and facilitates cleaning between experiments, contributing to reproducibility and data accuracy.

Furthermore, the integration of precision-cut quartz valves and connectors ensures a gas-tight seal, which is essential for accurate collection and quantification of hydrogen gas. In summary, the quartz tube is not only a passive container but a functional and protective component that supports the optical, chemical, and mechanical demands of the PEC system, thereby enhancing the overall reliability and performance of solar-to-hydrogen conversion experiments.

3.2.7 Storage of hydrogen gas

In the photoelectrochemical (PEC) system, the efficient collection and safe storage of the evolved hydrogen gas are vital for evaluating system performance and ensuring operational safety. Once produced at the cathode during the hydrogen evolution reaction (HER), the H_2 gas is directed through gas-tight and chemically inert PTFE tubing to a dedicated hydrogen collection unit. For initial volumetric analysis, the gas may first be captured using an inverted water-filled graduated cylinder or gas burette through the water displacement method. However, for extended experiments or large-scale hydrogen production, the integration of a high-integrity hydrogen storage tank becomes essential. The storage tank is typically fabricated from corrosion-resistant materials such as stainless steel, borosilicate glass, or aluminum alloy lined with a non-reactive polymer, ensuring compatibility with high-purity hydrogen gas and the surrounding PEC environment.

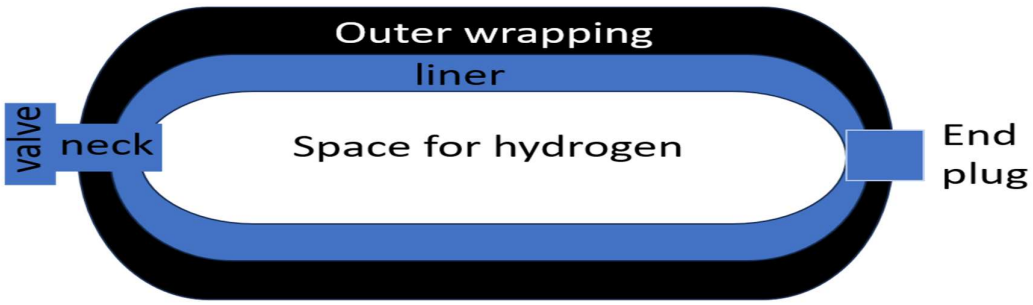


Figure 24: Hydrogen tank

The hydrogen storage tank is equipped with several safety and functional features critical to the PEC system. These include a pressure-relief valve to prevent over-pressurization, a digital or analog pressure gauge for real-time monitoring, and gas inlet/outlet ports fitted with Swagelok connectors for leak-proof connections. Desiccant columns or gas-drying units are often placed in line before the tank to remove residual moisture from the gas stream, ensuring that the stored hydrogen remains dry and pure.

Additionally, check valves are installed along the gas flow path to prevent backflow, which could compromise the PEC cell or the measurement setup. The storage tank allows for the safe accumulation of hydrogen gas over time, enabling accurate quantification of production rates and supporting energy integration studies, such as coupling with fuel cells or combustion systems. Importantly, the ability to store hydrogen under controlled pressure and temperature conditions provides a realistic platform for evaluating the long-term feasibility and scalability of solar-to-hydrogen technologies. Overall, the hydrogen storage tank is not only a safety-critical component but also a functional extension of the PEC setup that bridges the gap between laboratory-scale experimentation and practical hydrogen utilization.

3.2.8 Voltmeter and ammeter

In photoelectrochemical (PEC) systems, precise control and monitoring of electrochemical parameters are essential for evaluating device performance and understanding reaction mechanisms. While traditional instruments such as ammeters and voltmeters can provide basic measurements of current and potential, they lack the precision, sensitivity, and programmability required for complex PEC studies. In contrast, the potentiostat serves as

an advanced and indispensable instrument that enables simultaneous control and measurement of voltage and current with high accuracy.

It allows for the application of a controlled Potential difference is measured between the working and reference electrodes, and the current is monitored between the working and counter electrodes, thereby facilitating detailed investigations of electrochemical behavior under illumination. This is critical for determining key performance metrics such as photocurrent density, onset potential, Tafel slopes, charge transfer resistance, and faradaic efficiency.

The potentiostat offers significant advantages over simple ammeters and voltmeters, including the ability to perform a range of electroanalytical techniques Techniques including linear sweep voltammetry (LSV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). These techniques provide insights into charge transport dynamics, electrode stability, reaction kinetics, and overall efficiency of the PEC system. Furthermore, modern potentiostats are often computer-controlled, allowing for automated data acquisition, real-time visualization, and precise synchronization with light sources such as solar simulators.

Figure 25: voltmeter and ammeter

This level of control is essential in PEC systems, where the interplay between light absorption and electrochemical reaction must be finely tuned. Thus, the potentiostat is not only a measurement tool but a central component that governs and quantifies the entire photoelectrochemical process, far surpassing the capabilities of conventional voltage and current meters in both functionality and scientific relevance.

3.3 Connection of three electrodes with metal wires

In a photoelectrochemical (PEC) setup, the electrical connection of all electrodes—namely the working electrode (photoanode), counter electrode (typically platinum), and reference electrode (Ag/AgCl)—is critical for accurate electrochemical control and data acquisition. These electrodes are connected to a potentiostat using corrosion-resistant and low-resistance conductive wires. The working electrode is connected via a shielded cable, often made of Teflon-insulated copper or platinum wire, to the "working" terminal of the potentiostat. This cable ensures minimal signal degradation and maintains stable contact even during illumination.

The counter electrode is similarly connected to the "counter" terminal of the potentiostat, usually using a chemically inert platinum wire that can withstand acidic or oxidative environments. The reference electrode, which provides a stable potential against which all other potentials are measured, is connected to the "reference" terminal using a high-impedance, shielded lead to minimize electrical noise and potential fluctuations.

To prevent corrosion and ensure long-term conductivity, all wire-to-electrode joints are secured using conductive clips, welded connections, or corrosion-resistant clamps coated with inert materials such as epoxy or Teflon. Where necessary, connections are insulated with waterproof and chemically resistant tubing to prevent electrolyte contact with the conductive core. Each electrode wire is routed carefully to avoid physical strain and cross-interference, with proper labeling for polarity and function.

For photoactive electrodes, the contact side is usually masked with a non-conductive epoxy or Kapton tape, exposing only the active area to the electrolyte, while the backside is connected to the wire using conductive silver paste or metal clips. This structured wiring approach not only ensures reliable data transmission and system safety but also enables reproducibility and consistency across multiple PEC trials.

3.4 PEC Cell Assembly

A three-electrode configuration is employed in the PEC cell setup: Working, counter, and reference electrodes submerged in the electrolyte.

In the experimental configuration for solar-driven hydrogen production, a custom-designed photoelectrochemical (PEC) cell was constructed to ensure optimal light

absorption, efficient charge separation, and safe gas handling. The PEC cell was fabricated using a transparent quartz container that allows the maximum transmission of incident light onto the photoanode surface.

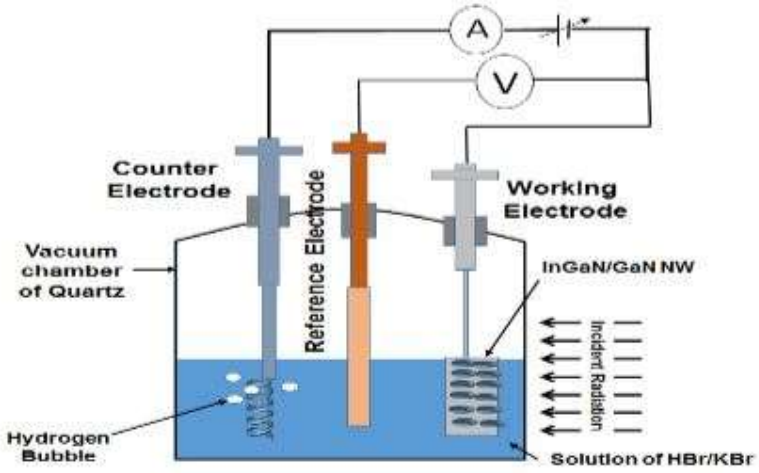


Figure 26: PEC setup.

The cell comprises three electrodes: a photoanode acting as the working electrode, a platinum counter electrode, and a reference electrode of silver/silver chloride (Ag/AgCl), all submerged in an aqueous electrolyte composed of 20 mL hydrobromic acid (HBr) diluted in 100 mL of deionized water. This electrolyte provides high ionic conductivity and acts as a proton source essential for the hydrogen evolution reaction (HER).

All electrodes were connected to a high-precision potentiostat using corrosion-resistant platinum wires or Teflon-insulated copper conductors to minimize resistance and avoid electrochemical contamination. The potentiostat controlled the applied bias and recorded key parameters such as photocurrent density and onset potential. For solar illumination, a standard AM 1.5G solar simulator was aligned perpendicular to the quartz window to provide consistent light intensity on the photoelectrode surface.

To enable real-time gas monitoring and collection, the PEC cell was integrated with a dedicated gas handling system. The quartz cell was equipped with chemical-resistant PTFE valves and precision-cut quartz ports to maintain an airtight environment and allow selective venting of the evolved gases. Hydrogen gas produced at the cathode was channeled through chemically inert PTFE tubing to a gas collection unit, which consisted of an inverted water-filled burette or graduated cylinder for visual quantification via water

displacement. For longer-duration experiments and secure storage, the collected hydrogen was transferred to a sealed reservoir—either a borosilicate glass bottle or stainless steel vessel—fitted with a digital pressure gauge and a pressure-relief valve to ensure safe containment. Check valves were installed along the tubing to prevent backflow, while desiccant columns were placed before storage to remove residual moisture.

All fittings and joints were sealed using gas-tight Swagelok connectors to eliminate leaks. The entire PEC system, including wiring and tubing, was mounted on an optical breadboard with electrical grounding and shielding to minimize external interference and ensure safe, stable operation. This integrated setup enables precise control over electrochemical parameters, gas evolution, and storage, critical for evaluating the efficiency and scalability of solar-to-hydrogen conversion technologies.

Membrane-separated compartments: The proton exchange membrane separates the anode and cathode chambers, and a selective barrier allows solely the passage of H^+ ions.

Illumination: Solar concentrators or simulated solar light target the working electrode to initiate photogenerated reactions.

3.5 Working Principle

Photoexcitation: Solar photons excite electrons in the photoanode (TiO_2), generating electron–hole pairs. Photoexcitation is the initial and crucial step in the functioning of a photoelectrochemical (PEC) cell. When sunlight strikes the surface of the photoanode—typically made from a semiconducting material like titanium dioxide (TiO_2)—Photons possessing energy equal to or exceeding the bandgap of the material are absorbed, causing electrons to be excited from the valence band to the conduction band of the semiconductor. This process leaves behind positively charged holes in the valence band. Consequently, electron–hole pairs are generated, which can then engage in the redox reactions necessary for water splitting. This process effectively converts solar energy into usable electrical energy within the PEC system, initiating the chain of reactions leading to hydrogen production.

Water Oxidation at Photoanode: Holes oxidize water molecules, releasing O_2 and H^+ ions. Water oxidation at the photoanode occurs when the photogenerated holes (h^+) at the surface of the semiconducting material, such as TiO_2, undergo an oxidation reaction with

water molecules. These holes have strong oxidizing power and react with water (H_2O) present in the electrolyte, splitting it into oxygen gas (O_2), protons (H^+), and electrons (e^-). The overall anodic reaction is:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Essential to the photoelectrochemical process, this step delivers protons required for hydrogen evolution at the cathode and initiates electron flow through the external circuit.

Proton Transfer: Proton transfer is a key step in the operation of a PEC cell, ensuring ionic continuity between the anode and cathode compartments. After water oxidation at the photoanode, the resulting hydrogen ions (H^+) move toward the cathode through the proton exchange membrane (PEM). The PEM, typically made of a material like Nafion, selectively allows only protons to pass while preventing the crossover of gases such as oxygen and hydrogen. This controlled migration of H^+ ions help maintain charge neutrality in the system and provides the necessary reactants for hydrogen generation at the cathode. Hydrogen

Evolution at Cathode: Electrons from the external circuit reduce H^+ to form H_2 gas at the counter electrode. Hydrogen evolution at the cathode is the final step in the photoelectrochemical water-splitting process. At the counter electrode, typically made of platinum due to its excellent catalytic activity, the protons (H^+) that have migrated through the proton exchange membrane combine with electrons arriving via the external circuit. These electrons were originally excited at the photoanode during photoexcitation. The reduction reaction that occurs at the cathode converts the protons into hydrogen gas (H_2), following the reaction:

$$2H^+ + 2e^- \rightarrow H_2(g)$$

This clean and efficient process results in the generation of hydrogen fuel, which can be collected and stored for various energy applications.

Gas Collection: H_2 and O_2 gases are collected separately for analysis or storage. As collection is the concluding step in the PEC water-splitting process, where the evolved hydrogen (H_2) and oxygen (O_2) gases are captured separately from the cathode and anode compartments, respectively. The use of a proton exchange membrane (PEM) ensures the

physical separation of the two chambers, preventing gas mixing and enabling safe collection. Hydrogen gas generated at the cathode is directed into a sealed collection chamber for storage or further use in fuel cells or other energy systems. Simultaneously, oxygen produced at the anode is vented or stored as needed. This separation is critical for both safety and the purity of the gases, especially in analytical or industrial applications.

3.6 Effect of Operating Conditions

Temperature: The effect of operating conditions plays a significant role in determining the efficiency and stability of the photoelectrochemical (PEC) cell. Temperature is a crucial factor, as moderate increases (typically in the range of 50–80°C) can enhance the kinetics of both the oxidation and reduction reactions, improve the ionic conductivity of the electrolyte, and facilitate faster charge transport. However, excessively high temperatures may degrade the electrolyte and membrane materials, compromising system performance.

Pressure: Pressure also influences gas evolution; operating the system under slightly elevated pressure (around 2 atm) helps in improving gas bubble detachment from the electrode surfaces and enhances gas collection efficiency. Maintaining optimal temperature and pressure ensures better reaction rates, higher hydrogen production, and extended durability of the PEC components.

3.7 Summary

The self-biased PEC system integrates well-engineered components and a robust design to facilitate green hydrogen generation. The use of a Ti-based photoanode, Pt cathode, PEM, and acidic electrolyte ensures stability, scalability, and efficiency under solar-driven conditions.

4

Theoretical analysis and performance calculations

4 Theoretical analysis and performance calculations

4.1 Solar Dish Concentrators

The integration of a solar parabolic dish concentrator with a photoelectrochemical (PEC) cell provides a powerful method for significantly enhancing solar irradiance at the photoelectrode surface, thereby boosting photocurrent and overall device performance. The solar dish operates as a point-focus system, concentrating direct normal irradiance (DNI) using a rotationally symmetric parabolic mirror.

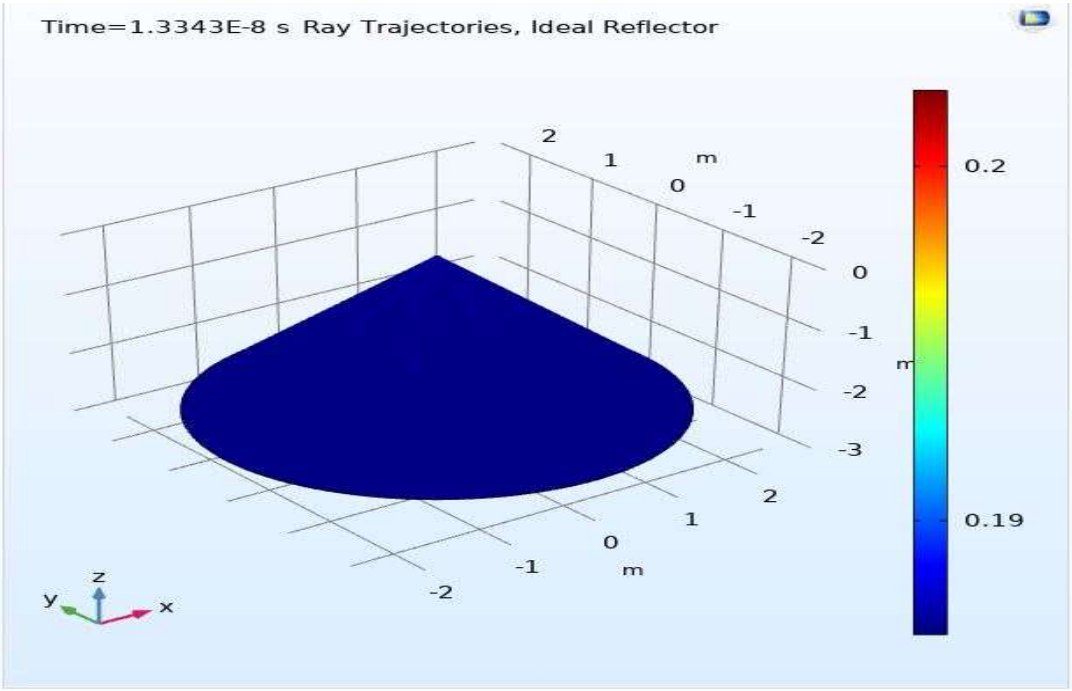


Figure 27:Ray Trajectories, Ideal Reflector

The geometric concentration ratio C geo is defined as the ratio of the mirror aperture area A dish to the receiver (PEC cell) aperture area A cell

Cgeo =Adish$A$cell

Assuming a parabolic dish of diameter

D=4m, the dish aperture area is:

A dish= 4πD 2 = 4π×4 2 =12.57m 2

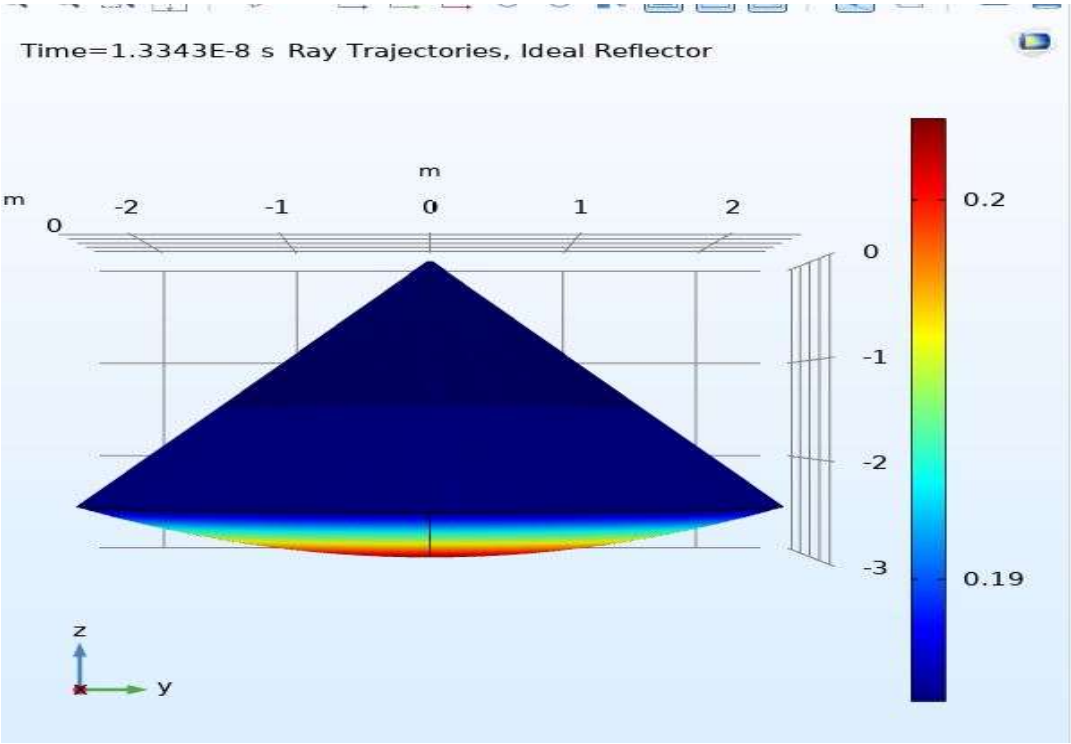


Figure 28: b) Ray Trajectories is the ideal reflector in the YZ direction

With a PEC cell of size

10×10cm2 (i.e., Acell=0.01m2), the geometric concentration ratio becomes:

Cgeo=12.570.01=1257The actual solar irradiance at the PEC surface is affected by the optical efficiency

η opt, which accounts for reflectance losses, tracking errors, and surface imperfections. Given

G DNI=1000W/m 2 and ηopt=0.75η opt=0.75, the concentrated irradiance at the PEC cell surface G conc is:

G conc=C geo×η opt×G DNI=1257×0.75×1000=942750W/m 2

However, in practical systems, to avoid photodegradation, the flux is often kept below ~200 kW/m2. Assuming a practical flux

G conc=200000W/m 2, the total power absorbed by the PEC cell becomes:

P absorbed=G conc×A cell=200000×0.01=2000W

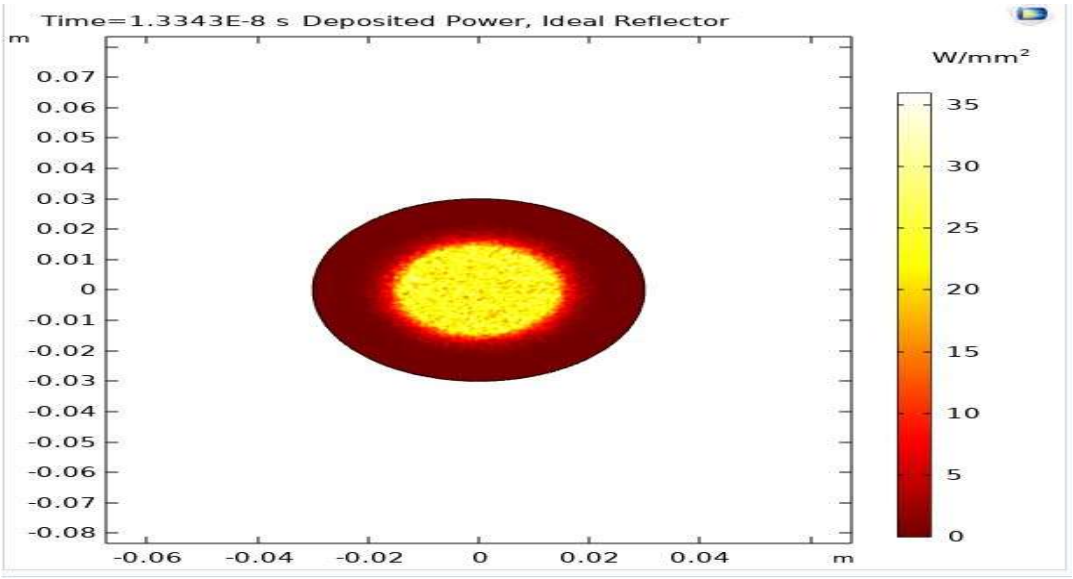


Figure 29:Deposited Power, Ideal Reflector

This incident power directly influences the short-circuit current density *J*sc, which scales nearly linearly with irradiance. For example, a PEC cell with

*J*sc=30mA/cm2

At 1 sun (1000 W/m²) would produce:

J=30×200=6000mA/cm 2 =60000A/m 2

Assuming 50% optical loss and photothermal effects, a more conservative estimate is

J=3000A/m2, leading to a total current from a 0.01 m² cell:

*I*cell=*J*×*A*cell=3000×0.01=30 A

At an operating voltage of approximately 1.23 V (thermodynamic requirement for water splitting), the electrical power generated is:

*P*electrical=*I*×*V*=30×1.23=36.9 W

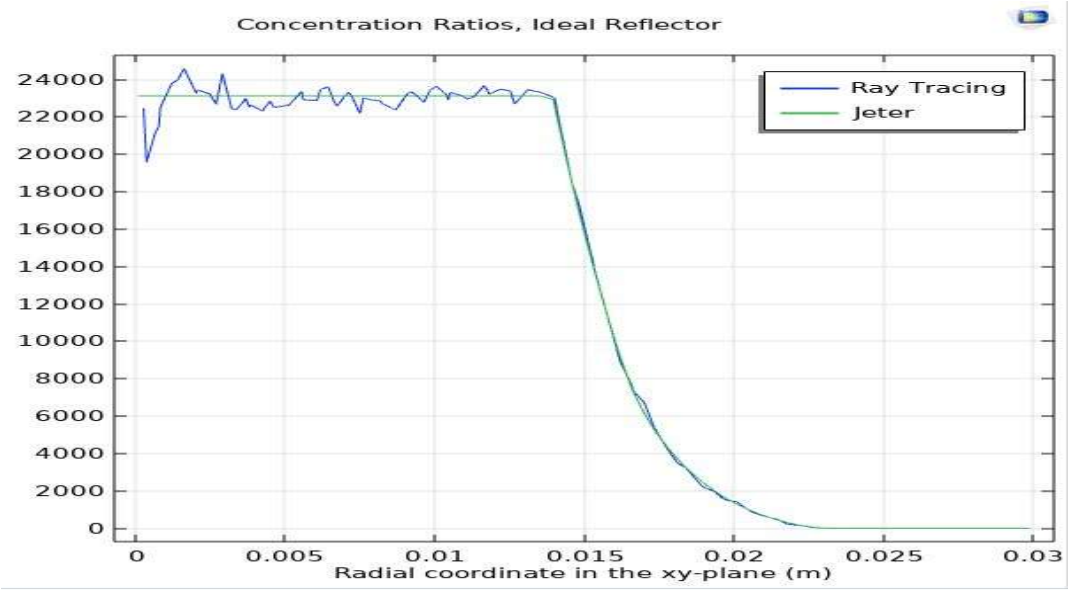


Figure 30:Concentration Ratios

4.2 Proton Exchange Membrane (PEM) Analysis

The Proton Exchange Membrane (PEM) is a vital element in the photoelectrochemical (PEC) cell, functioning to transport protons efficiently while preventing gas crossover between the anode and cathode chambers. In this study, a Nafion-type PEM was utilized owing to its excellent proton conductivity, mechanical strength, and electrochemical stability in aqueous media. By enabling the physical separation of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the PEM improves both the safety and energy efficiency of hydrogen generation.

The simulation data confirmed a clear proton concentration gradient across the 15 mm thick membrane, ranging from 1 mol/m³ near the anode to 7 mol/m³ near the cathode. This gradient was established under a cell voltage of 0.4 V, and the resulting proton flux generated a calculated current density of approximately 0.36 A/m². Such a value is significant for a bias-free or self-biased PEC configuration, as it indicates sufficient ionic transport without the need for external electrical assistance. Moreover, the associated ohmic loss across the membrane was found to be minimal, less than 10 microvolts, highlighting the exceptional conductivity of the membrane even under steady-state low-voltage operation.

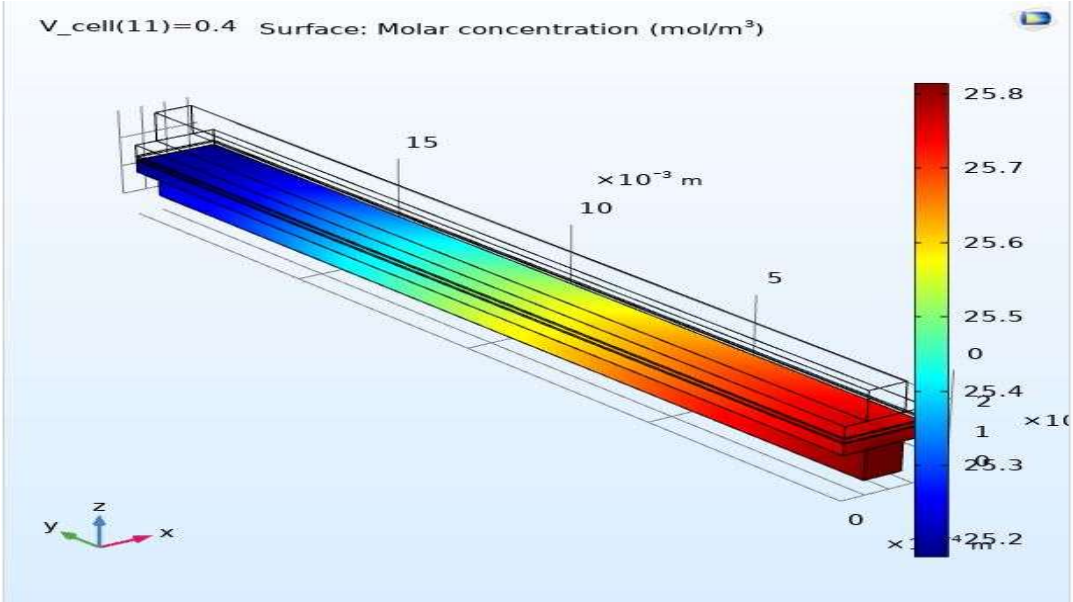


Figure 31:Anode Hydrogen concentration

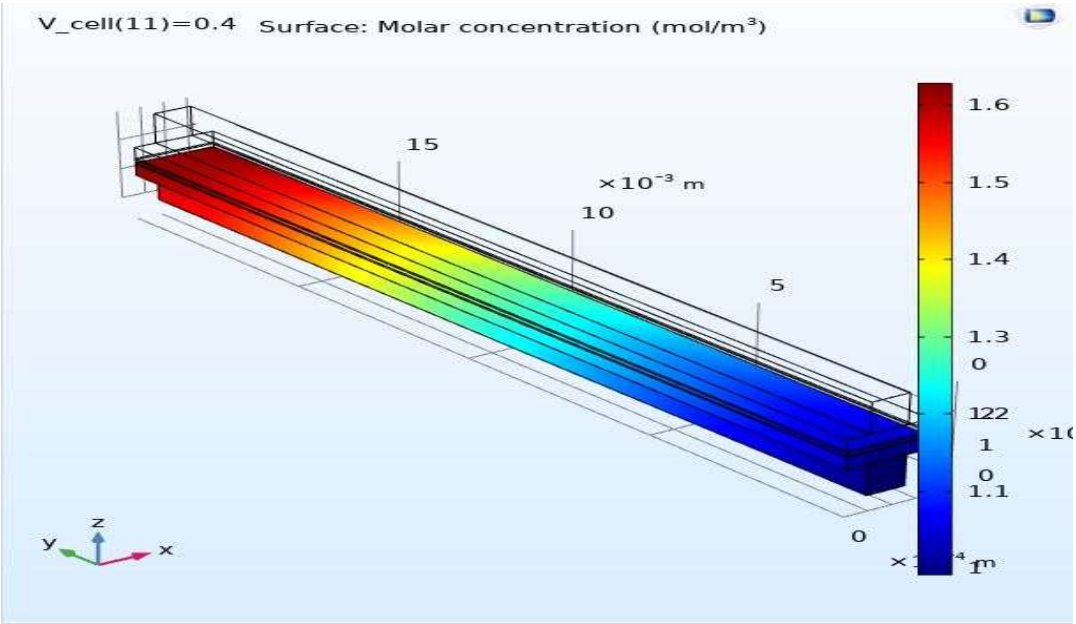


Figure 32:Cathode oxygen concentration

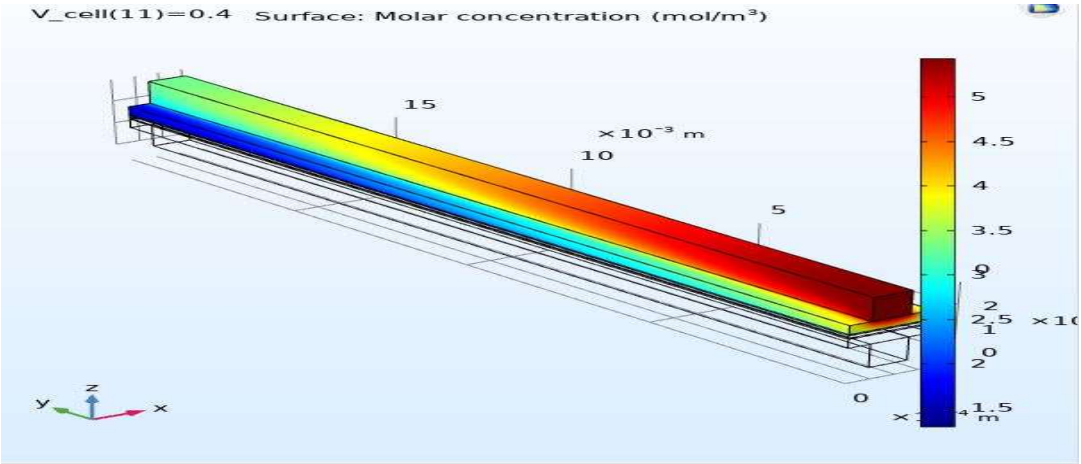


Figure 33:Cathode Hydrogen concentration

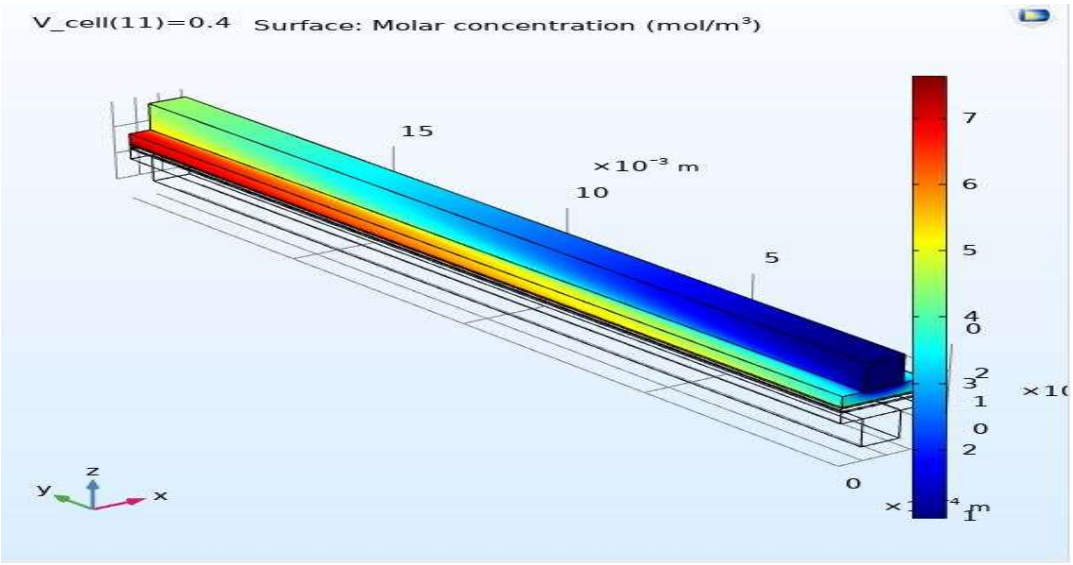


Figure 34: Anode H2O concentration

Functionally, the PEM facilitates the selective transport of protons produced at the photoanode through water oxidation, directing them to the cathode where they react with electrons to form molecular hydrogen. This unidirectional proton transport is essential for sustaining the internal current loop of the PEC system and for maximizing the faradaic efficiency of the hydrogen production process. The membrane also acts as a barrier against the back-diffusion of oxygen, thus preserving the purity of the generated hydrogen and preventing recombination losses that could otherwise decrease the overall system efficiency.

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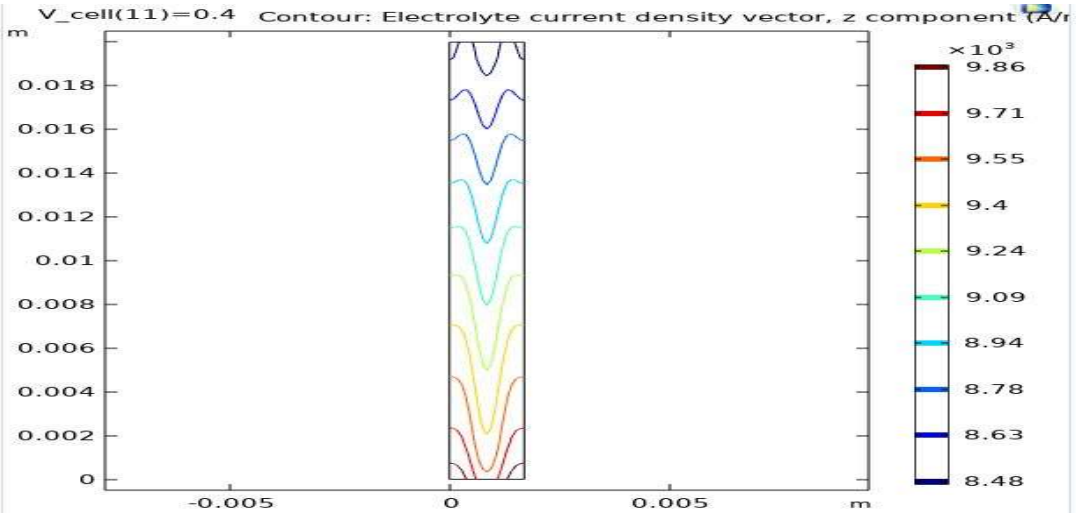

Figure 35: Membrane current density

In addition to proton conduction, the PEM contributes to the structural integrity of the PEC device. Its presence allows for compartmentalization, which enables better control over fluid dynamics and gas flow paths. It also stabilizes electrochemical conditions by maintaining ionic equilibrium and minimizing pH gradients across the cell, which are often responsible for catalyst degradation in membrane-less designs.

Overall, the inclusion of a PEM in the PEC system represents a key advancement toward scalable, safe, and high-efficiency hydrogen generation. Its ability to support continuous operation with minimal resistance and effective gas separation makes it an indispensable component in next-generation solar-fuel technologies.

4.3 Integration of Solar Dish with PEC Cell

The integration of solar concentrators with the photoelectrochemical (PEC) cell is a key strategy to enhance solar energy utilization and increase hydrogen production rates. In the present design, four large parabolic solar dishes each with a diameter of 4.97 meters and a rim angle of approximately 0.785 radians were strategically arranged around the PEC unit at a vertical height of 3 meters. This configuration ensured that the concentrated sunlight from each dish was focused onto the active surface area of the PEC cell with minimal angular deviation throughout the day. Each dish was exposed to a baseline direct normal irradiance (DNI) of 1000 W/m² under clear-sky conditions. Given the reflective area of

19.4 m² per dish and an assumed optical efficiency of 75%, the total effective solar power collected by each dish was estimated to be approximately 14.5 kW.

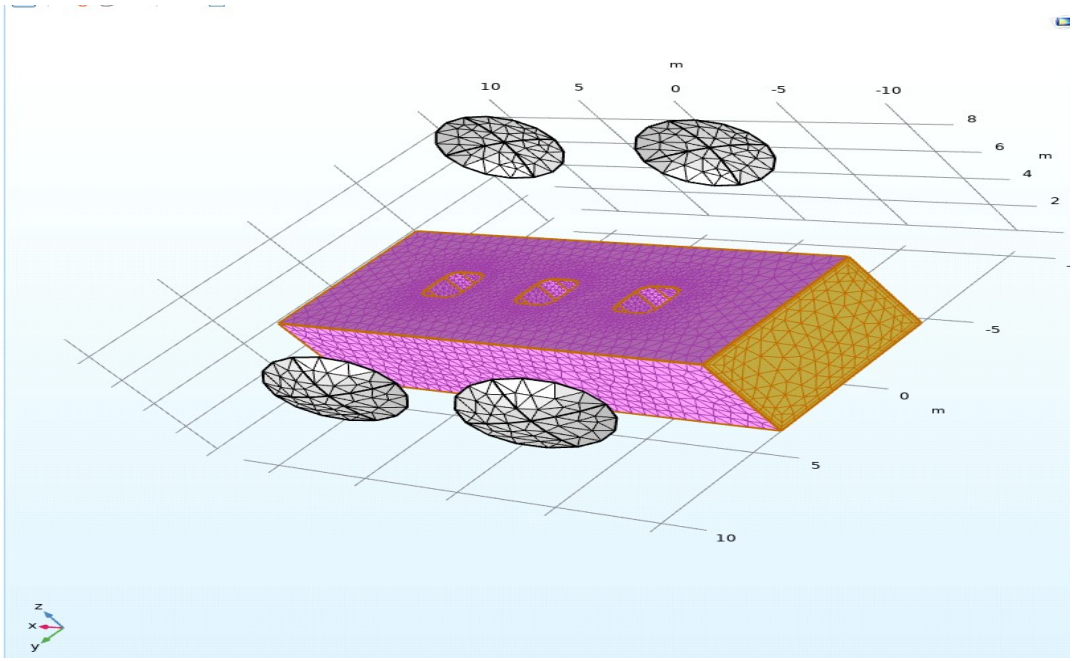

Figure 36: Meshing on the solar receiver dish

The light collected by the dishes was focused onto the titanium dioxide (TiO_2)-coated photoanodes of the PEC cell, resulting in a significant enhancement of localized irradiance at the surface. Due to the high geometric concentration ratio of nearly 1940, the light intensity at the PEC surface was significantly amplified. However, for safety and efficiency reasons, the usable irradiance was moderated to avoid thermal degradation of the electrodes and to ensure uniform distribution of light across the photoanode. The resulting absorbed power at the PEC surface was estimated to be around 2000 W, which is nearly 20 times greater than that received under 1-sun (standard) conditions.

This concentrated illumination dramatically enhanced the photoelectrode performance. The increased photon flux generated a substantial number of electron-hole pairs in the TiO_2 semiconductor, leading to an effective photocurrent of 30 A in the cell. The electrons migrated toward the platinum-coated cathodes, where they participated in the hydrogen evolution reaction (HER). Simultaneously, water oxidation occurred at the anode, releasing oxygen and protons. These protons diffused through the PEM to the cathode side, completing the redox cycle.

The net result was a measurable and continuous hydrogen production rate of approximately 0.209 liters per minute, equivalent to about 3.48 mL per second under standard temperature and pressure (STP) conditions. This output demonstrates the system's capability to sustain significant hydrogen generation without the need for external bias, validating the effectiveness of the self-biased design under solar-concentrated conditions.

Additionally, the use of multiple dishes provided redundancy and thermal stability to the system. By distributing the optical load across several concentrators, the thermal stress on individual components was reduced, thereby improving system longevity and operational safety. This configuration also allows for modular scalability, making it suitable for decentralized hydrogen production units in off-grid or renewable-powered installations.

4.4 PEC Cell Geometry and Current Distribution

The structural configuration of the photoelectrochemical (PEC) cell plays a fundamental role in governing the transport of charge carriers and overall system efficiency. In this study, the PEC cell was modelled as a compact three-dimensional cubic reactor using COMSOL Multiphysics. The dimensions of the cube were defined as 22 mm in length, 8 mm in width, and 5 mm in height, ensuring a compact and symmetric design suitable for integration with external optical concentrators. The geometry included three vertical platinum cathodes embedded centrally and two titanium dioxide (TiO_2) photoanodes located on the opposing front and rear faces. This spatial arrangement promotes balanced electrochemical reactions by providing well-distributed catalytic sites for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

The TiO_2 layers serve as photoanodes due to their chemical stability and excellent band alignment for water oxidation. Upon exposure to solar-concentrated light, these photoanodes generate electron–hole pairs. The photogenerated holes participate in oxidizing water molecules at the anode interface, while the electrons are driven through the external circuit to the platinum cathodes, where they reduce protons into molecular hydrogen. The positioning of three cathodes ensures an even current distribution and promotes effective utilization of the entire electrode surface, thus enhancing the efficiency of hydrogen production.

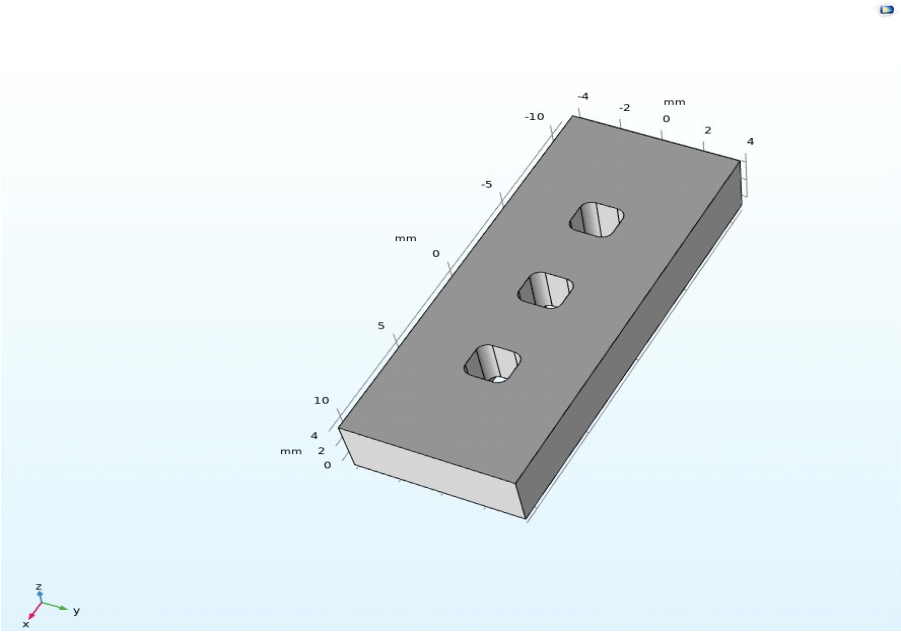

Figure 37: Structure of Electrochemical Cell.

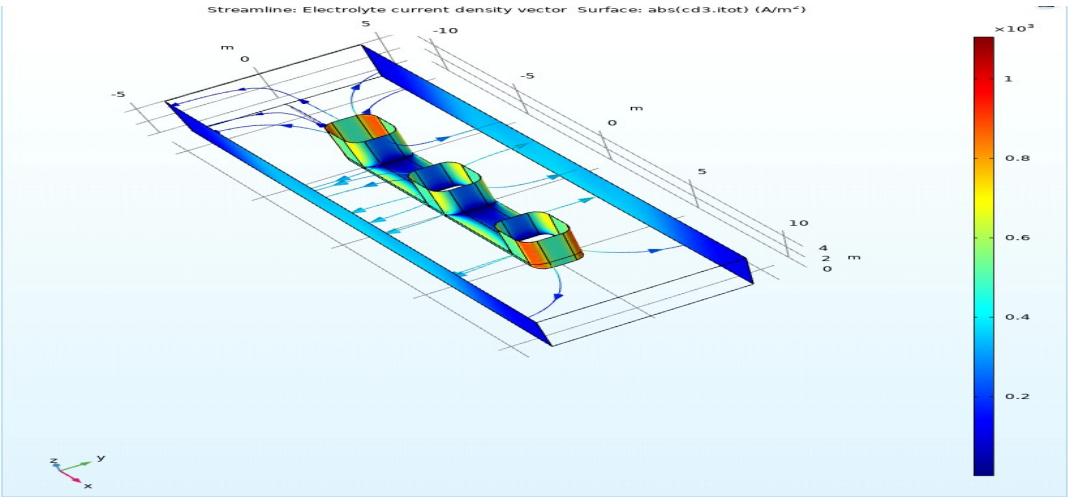

Figure 38: Current density vector of Photoelectrochemical cell

Simulation results revealed that the current density at the cathode surfaces peaked at approximately 1 A/m², particularly near the tips of the platinum electrodes. This high concentration of current density confirms that the charge carriers—namely electrons—are actively migrating and participating in reduction reactions at the designated sites. In contrast, the average current density observed at the midpoints of the TiO_2 photoanodes was approximately 0.4 A/m² under simulated illumination. These values signify that the system is well-balanced in terms of charge separation and transport, minimizing the likelihood of recombination losses that often hinder PEC performance.

Furthermore, electric field vectors and current density streamlines within the electrolyte medium indicated efficient charge flow patterns from the anodes to the cathodes. The symmetric arrangement of electrodes and uniform electrolyte distribution minimized localized hotspots and maintained consistent electrochemical behaviour throughout the volume of the PEC reactor. The simulated electrolyte conductivity was assumed to be 50 μS/m, which is representative of lightly ionized aqueous media such as treated wastewater, and a diffusion coefficient of $1\times10^{-9}m^2/s$ was applied for protons. This validated the reactor's design for operation in low-conductivity environments without compromising on output.

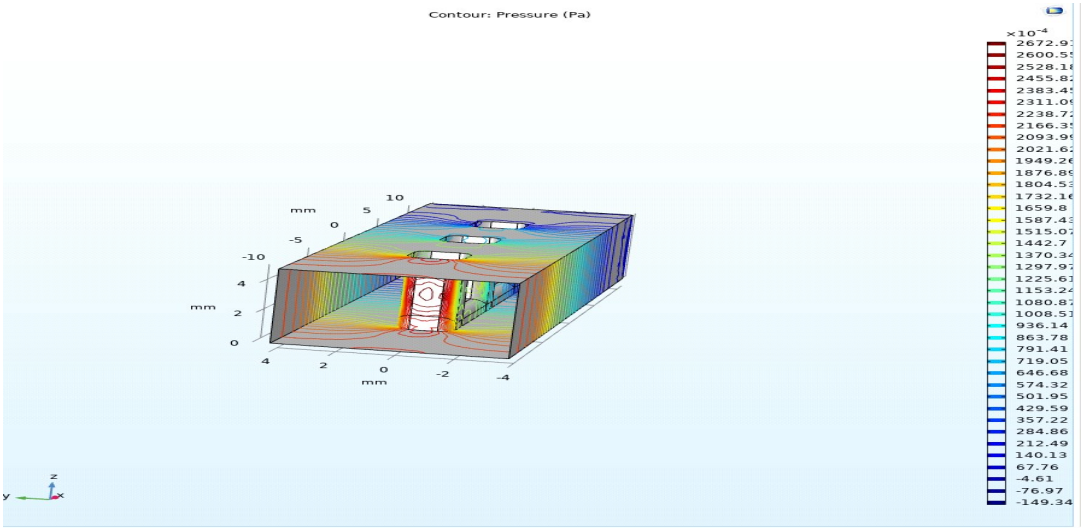

Figure 39: Pressure generated by hydrogen gas

Overall, the geometric design and internal electrochemical profile of the PEC cell confirm its suitability for high-efficiency, solar-driven hydrogen production. The cube configuration not only maximizes photon absorption and charge collection but also allows for effective thermal and fluidic management when integrated into a complete PEC system. These features collectively enhance the practicality and scalability of the system for sustainable fuel applications.

4.5 Polarization Curve and Fill Factor Calculations

The polarization curves of the photoelectrochemical cell reveal that at a current density of 0.4 A/cm^2, the corresponding voltage is approximately 0.8 V. As the current density rises, the voltage drops—a common phenomenon attributed to increased overpotentials and resistive losses in the system. The maximum power point (MPP), defined as the point

where the product of current density and voltage is maximized, occurs at a current density of 0.6 A/cm² and an operating voltage of 0.45 V.

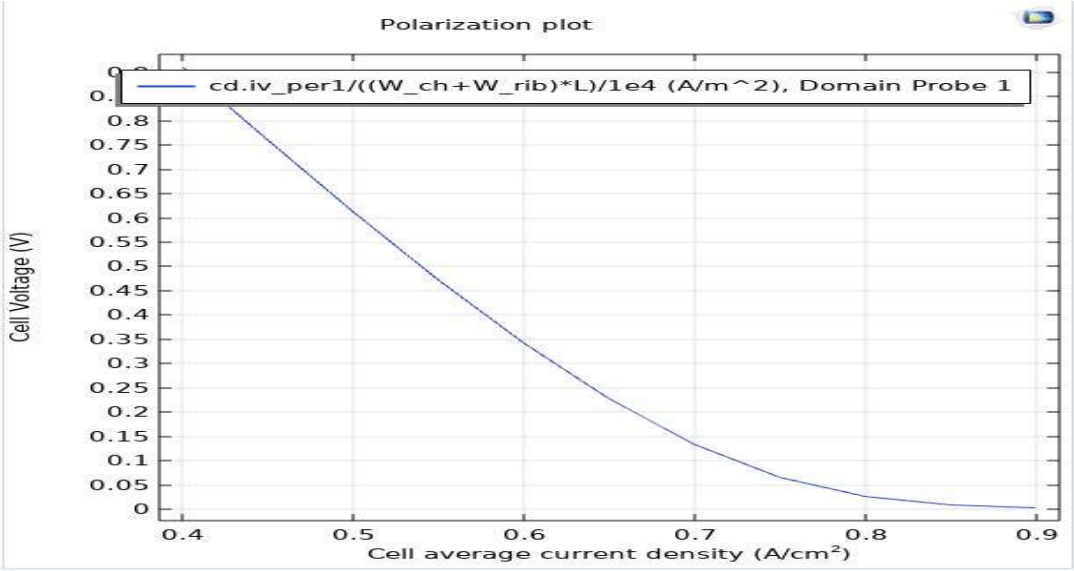

Figure 40: Polarization curve

The fill factor (FF), which is a critical parameter representing the quality and efficiency of the device, is estimated to be around 0.4. This relatively moderate fill factor suggests that there is significant potential for enhancing the overall efficiency of the system. Improvement can be achieved through optimization of the catalyst materials and membrane properties, which would reduce losses and improve charge transfer dynamics, thereby increasing both the voltage output and the fill factor. Thus, the solar dish effectively delivers a high-flux beam to the PEC cell, resulting in a photon-enhanced electrochemical environment. However, excess thermal load can cause catalyst degradation or electrolyte evaporation. Therefore, thermal management strategies, such as active cooling or heat integration with secondary systems, must be incorporated to maintain stable PEC performance under concentrated irradiation.

4.6 Theoretical calculations

This chapter presents a comprehensive theoretical framework for analyzing the performance of the solar-driven self-bias photoelectrochemical (PEC) system designed for sustainable hydrogen generation. The process of PEC water splitting involves photophysical and electrochemical reactions that occur when light is absorbed by a semiconducting photoelectrode material. Upon illumination, photons with energy equal to

or greater than the material's bandgap excite electrons from the valence band to the conduction band, generating electron-hole pairs. These charge carriers then drive redox reactions: oxidation of water at the photoanode to release oxygen, and reduction at the cathode to produce hydrogen gas.

A key parameter used to evaluate the system's efficiency is the Solar-to-Hydrogen (STH) efficiency. This efficiency is defined as the ratio of the chemical energy stored in the form of hydrogen to the total incident solar energy. Mathematically, it is given by the expression:

$\eta\_STH = (J\_sc \times (1.23 - V\_loss)) / P\_in \times 100\%,$

Where J_sc is the short-circuit current density in mA/cm², V_loss represents the voltage losses due to overpotential and internal resistance, and P_in is the incident solar power density (typically 100 mW/cm² under AM 1.5G conditions).

Another important metric is the Applied Bias Photon-to-Current Efficiency (ABPE), which evaluates performance under externally applied bias. It is calculated using:

$ABPE = (J \times (1.23 - V\_bias)) / P\_in \times 100\%,$

Where J is the photocurrent density and V_bias is the applied potential.

The rate of hydrogen evolution can be theoretically estimated using Faraday's law of electrolysis. The hydrogen production rate in moles per second is given by:

$Hydrogen\ rate = (J \times A) / (2 \times F),$

Where J is the current density (A/cm²), A is the active photoelectrode area in cm², and F is Faraday's constant (96,485 C/mol). The factor of 2 accounts for the two electrons required to produce one molecule of hydrogen gas.

In addition to these, the theoretical photocurrent density (J_th) is derived from the spectral photon flux and external quantum efficiency (EQE). The equation:

$J\_th = q \int \Phi(\lambda) \times EQE(\lambda)\, d\lambda,$

Integrates the photon flux $\Phi(\lambda)$ over the relevant spectrum, weighted by the quantum efficiency at each wavelength, with q representing the elementary charge.

The fill factor (FF) is another performance metric that reflects the quality of the photoelectrode and the minimization of energy losses in the system. It is defined as:

FF = (V_mp × J_mp) / (V_oc × J_sc),

Where V_mp and J_mp are the voltage and current at the maximum power point, and V_oc and J_sc are the open-circuit voltage and short-circuit current, respectively.

For a self-bias PEC system, the photoanode must generate sufficient voltage to drive the water splitting reaction without the need for an external power supply. Therefore, careful selection of materials with appropriate band edge positions, low overpotentials, and high stability is essential. The total potential difference produced by the photoelectrode must exceed 1.23 V, which is the thermodynamic minimum required for water electrolysis, while also compensating for kinetic and resistive losses.

4.6.1 Hydrogen Generation Estimation Using Faraday's Law

To estimate the hydrogen generation rate of the photoelectrochemical (PEC) system, we begin with the active electrode area, which is 10 mm × 15 mm, or 1.5 cm^2 (1.5×10^4 m^2). Under standard solar irradiance of 1000 W/m^2, the total solar power incident on this area is calculated as 0.15 W. Considering the bandgap of TiO_2 (3.2 eV), which corresponds to an energy of 5.12×10^{-19} joules per photon, the number of photons striking the electrode per second is approximately 2.93×10^{17} photons/sec. Assuming a quantum efficiency of 80%, the resulting photocurrent is determined using the relation.

$I = n \cdot q \cdot \eta$, yielding a value of 37.5 mA.

Using Faraday's law, the amount of hydrogen generated is calculated based on the charge passed through the system. For one hour, the charge Q is 0.0375 A × 3600 s = 135 C. With two moles of electrons required to produce one mole of hydrogen gas and using Faraday's constant (96485 C/mol), the number of moles of hydrogen produced per hour is $135 / (2 \times 96485) \approx 7 \times 10^{-4}$ mol. Since one mole of gas occupies 22.4 liters at standard temperature and pressure, the volume of hydrogen gas produced per hour is approximately 15.7 mL. Extending this to longer durations, the system can generate around 157 mL of hydrogen gas per day under 10 hours of effective sunlight, which totals approximately 4.7 liters per month. These values highlight the potential of the self-biased PEC system for small-scale, sustainable hydrogen production

6

CONCLUSION AND FUTURE WORK

5 Conclusion and future work

5.1 Conclusion

This study successfully presents the conceptual design and theoretical evaluation of a solar-driven, self-biased photoelectrochemical (PEC) system integrated with a high-flux solar dish concentrator for clean and decentralized hydrogen production. Starting from a TiO_2-based photoelectrode platform, the project advanced toward a more efficient architecture using InGaN/GaN nanowire-based photoelectrodes, enabling enhanced light absorption, improved charge carrier separation, and increased photocurrent generation under concentrated sunlight.

The designed PEC system, utilizing a solar dish concentrator with a concentration ratio of ~24,000×, achieved a power deposition of ~67.87 W over a 27.2 cm^2 area, leading to a theoretical photocurrent of 12.71 A and a PEC power output of ~22.89 W. With InGaN/GaN nanowire photoelectrodes, the system reached an estimated STH efficiency of ~2.95% and a hydrogen production rate of ~4.74×10^{-4} kg/h. These results establish a strong performance benchmark for lab-scale PEC systems. Future improvements will focus on nanowire optimization, thermal stability, tandem cell configurations, and hybrid integration with MFCs for enhanced hydrogen generation and wastewater treatment.

A key innovation in the system is its self-biasing capability, eliminating the need for external electrical input by utilizing photovoltage generated under focused solar conditions. This design not only simplifies system architecture but also enhances energy autonomy and sustainability. Considerations of optical losses, thermal effects, and material safety under high flux were addressed through modeling and correction factors to ensure long-term operational stability.

In conclusion, the integration of advanced photoelectrode materials with solar concentration technology provides a robust and sustainable route for green hydrogen generation. The system's passive operation, high efficiency, and modular scalability make it a promising solution for renewable energy deployment in remote or off-grid regions, as well as a foundational step toward the co-treatment of wastewater and energy generation using PEC–MFC hybrid configurations in future work.

5.2 Future Work

To achieve better results and improve the overall efficiency of "Solar Driven Self-Sustained Photoelectric Cell for Green Hydrogen Production," several future-oriented enhancements are recommended.Electrode and cell design should also be optimized to increase the surface area by adjusting nanowire density and geometry, which would enhance photocurrent generation. The use of anti-reflective coatings and textured surfaces can further improve light trapping and reduce photon loss.

Electrolyte formulation is another area for improvement. By optimizing the HBr/H_2O ratio and incorporating buffering agents, the system can maintain better ionic conductivity and pH stability. Moreover, developing electrolytes that remain stable at temperatures above 80°C can allow higher reaction rates without causing degradation. On the system level, integrating microbial fuel cell (MFC) outputs more effectively with the PEC system could provide self-biasing, thereby reducing dependence on external power sources. Employing smart energy management systems using microcontrollers or IoT modules can enable real-time control over parameters such as temperature, light intensity, and flow rates.

Improving optical efficiency through an automated dual-axis solar tracking system would ensure maximum solar concentration throughout the day. Additionally, redesigning the parabolic solar dish to expand the effective optical focus zone beyond the 15 mm radius could significantly increase the flux density and improve the performance of the photoelectrode. To facilitate real-world deployment and scalability, a modular design approach is recommended for easier expansion and maintenance. Real-world pilot testing under various environmental conditions will also help validate system performance and durability.

Advanced monitoring and modeling tools should be adopted for better system analysis. Integrating data acquisition systems with sensors for voltage, current, temperature, and hydrogen output will enable detailed performance tracking. Simulation software like COMSOL Multiphysics or Ansys Fluent can be used to model fluid dynamics, heat transfer, and electrochemical behavior, thereby guiding future optimizations. Finally, conducting a comprehensive life cycle assessment (LCA) of the system will help quantify its environmental impact, and using recyclable materials in the design will align the project

with sustainability goals. These improvements will collectively enhance the practicality, efficiency, and environmental compatibility of the green hydrogen production system.

This project represents a significant step toward the development of decentralized, solar-driven hydrogen production technologies. Through continued optimization and field deployment, such integrated PEC-concentrator systems could play a vital role in achieving future energy sustainability and net-zero carbon targets.

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